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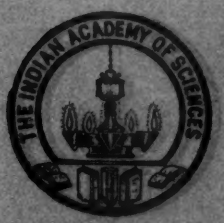

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THE HEAT CAPACITY OF DIAMOND BETWEEN 0 AND 1000° K.

By Sir C. V. Raman

(*Memoir No.* 103 *of the Raman Research Institute, Bangalore-6*)

Received November 14, 1957

1. Introduction

The evaluation of the heat capacity of diamond on the basis of the theory of specific heats of crystals advanced by the author formed the subject of a recent publication[1] in these *Proceedings*. Since then, fresh experimental determinations have been reported which go down to temperatures at which the value of C_p for diamond is as low as 0·0001, in other words only a fifty-thousandth part of its value 5·0 at 1000° K. which is itself smaller than the theoretical maximum of 5·96 for a monatomic solid. We proceed here to consider the new experimental results. The theoretical evaluation already published succeeds in explaining the change of C_p with temperature over the whole of this enormous range of values in a highly satisfactory manner, but with certain reservations made necessary by the fact that the theoretical calculations are based on the spectroscopic behaviour of ideal diamonds, whereas the reported determinations have been made with material which is very far indeed from being ideal. To exhibit the closeness of the agreement which is observed over practically the entire temperature range as well as the minor differences which are noticeable in certain limited parts of it, the data have been plotted on adequate scales alongside of the theoretical values in a series of graphs which are reproduced in the present paper. The cause of the small differences which appear in the temperature range between 50 and 150° K. is discussed and it is shown that they are explicable in terms of the differences in the spectroscopic behaviour of ideal and non-ideal diamonds.

Diamond illustrates in a most striking manner the fundamental relationship between the specific heats of crystals and their spectroscopic behaviour. Being an elementary solid crystallising in the cubic system with an exceptionally simple structure, the characteristic modes of atomic vibration which determine both the thermal behaviour and the spectroscopic properties of diamond can be described in geometric terms without any reference to the magnitude of the interatomic force constants. Considerations of a general nature enable us to go further and arrange these modes in a scale of descending frequency, thereby greatly facilitating their identification.

Diamond being a transparent solid, the modes and frequencies of atomic vibration in it are also accessible to observation by a variety of spectroscopic methods. It is found possible to determine these frequencies with precision and compare them with the theoretically computed values. Thus theory and experiment agree to give us a complete and detailed picture of the atomic vibration spectrum of diamond. It thereby becomes possible to evaluate the heat capacity of the crystal in a completely independent fashion involving no assumptions of any sort. The agreement which emerges between the results of such evaluation and the experimental data is a convincing demonstration of the correctness of the theoretical approach.

2. THE VIBRATION SPECTRUM OF DIAMOND

The crystal structure of diamond consists of two distinct sets of atoms of carbon which appear separately in layers parallel to the faces of the octahedron and the cube respectively. The normal modes of atomic vibration of the structure can be readily described in terms of this arrangement. The principal mode of vibration is an oscillation of the two sets of atoms with respect to each other along any one of the three cubic axes and has therefore a degeneracy of 3. The atoms present in the layers parallel to the octahedral faces may oscillate with respect to each other either normally or transversely to themselves with degeneracies of four and eight respectively; but since the adjacent non-equivalent layers may oscillate either in the same or opposite phases, we have two such sets of modes. Likewise, we have two sets of modes in which the layers of atoms parallel to the cube faces oscillate normally or transversely to themselves with degeneracies of three and six respectively. Thus, we have 9 distinct normal modes with degeneracies of 3, 4, 4, 8, 8, 3, 3, 6 and 6 respectively, making a total of 45 modes in all. Considering the set of 16 atoms contained in a volume element which is twice as large in each direction as the unit cell of the crystal structure, the total number of atomic degrees of freedom of this group is 48. The 45 modes of vibration described above may be regarded as the *modes of internal vibration of this group*, while the three degrees of freedom left over represent *its three translations.*

In a lecture on the diamond delivered at Zurich, Freiburg and Bonn in July 1956, and subsequently published in these *Proceedings*[2] it was shown in detail how the frequencies of the nine normal modes described above may be evaluated and checked against the frequency shifts observed in the scattering of light by diamond when it is traversed by the $\lambda 2536{\cdot}5$ radiations of the mercury arc. We shall content ourselves here with reproducing below as Fig. 1 a chart showing the nine frequencies and their respective degeneracies.

The two modes of oscillation normal to the cubic planes have an identical frequency of 1088 cm.$^{-1}$ They have accordingly been shown as a single frequency with a degeneracy of 6.

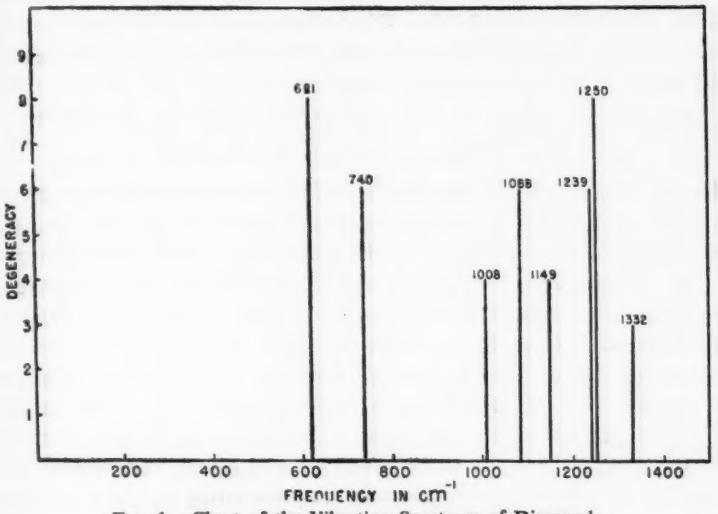

FIG. 1. Chart of the Vibration Spectrum of Diamond.

To complete the picture, we require to know how the three translatory movements of the 16-atom group manifest themselves in the vibration spectrum of the crystal. It is obvious that they would appear as internal vibrations in volume elements of larger size than the 16-atom group and therefore having lower frequencies. In dealing with vibrations of this nature, it is permissible to ignore the discrete atomic structure of the material. The larger the size of a volume element is, the lower would be the frequencies of its internal vibration. Considering volume elements of all possible sizes as the oscillators, their frequencies of internal vibration would evidently range from the lowest possible value $\nu = 0$ to an upper limit ν_L which may be taken equal to the lowest of the frequencies of vibration appearing in the chart (Fig. 1). The manner in which the disposable degrees of freedom of atomic movement are distributed over this range of frequencies is indicated by a simple argument. The number of volume elements of any specified dimension included in the crystal and hence also the number of degrees of freedom represented by their translations diminish in inverse proportion to the cube of the linear dimensions, while the frequencies of their internal vibration would vary inversely as the first power of the same. Hence the number of degrees of freedom appearing as internal vibrations of the volume

elements and having frequencies between 0 and ν would be proportional to ν^3. By differentiation, we obtain the result that the number of degrees of freedom appearing between frequencies ν and $\nu + d\nu$, in other words, the number of oscillators in the crystal having frequencies in that range would be proportional to $3\nu^2 d\nu$. The constant of proportionality may be deduced at once from the consideration that on integration between zero and the upper limit ν_L, we should obtain as the total number of oscillators three times the number of 16-atom groups comprised in the crystal.

3. THE HEAT CAPACITY OF DIAMOND

Having thus ascertained the nature of the complete vibration spectrum of diamond, we proceed to make use of the theory of Einstein and obtain an expression for the heat content of the crystal as a function of the temperature. This appears as a sum of two quantities; the first is a summation of the average energies of the individual oscillators having the discrete frequencies shown in the chart (Fig. 1) multiplied by their respective degeneracies and by the total number of 16-atom groups contained in the crystal. The second part is a summation of the average energies of vibration of the oscillators of larger sizes having various frequencies from 0 to ν_L, and this takes the form of an integral between these limits of frequency. The details of the calculations have already been given in the earlier paper and it is therefore sufficient to reproduce here the final results here in tabular form.

TABLE I

Theoretical Computation of the Atomic Heat of Diamond

(Calories per gram-atom per degree)

Absolute Temperature	Discrete Frequencies	Residual Spectrum	Total	Absolute Temperature	Discrete Frequencies	Residual Spectrum	Total
15°	..	0·00014	0·00014	200	0·4069	0·1631	0·5700
20	..	0·00033	0·00033	225	0·5894	0·1895	0·7789
25	..	0·00064	0·00064	250	0·7844	0·2124	0·9968
30	..	0·0011	0·0011	275	1·0137	0·2319	1·2456
40	..	0·0026	0·0026	300	1·2418	0·2486	1·4904
50	..	0·0051	0·0051	350	1·700	0·275	1·975
60	..	0·0088	0·0088	400	2·139	0·294	2·433
70	0·0005	0·0140	0·0145	450	2·538	0·308	2·846
80	0·002	0·0207	0·0227	500	2·892	0·319	3·211
90	0·0056	0·0290	0·0346	600	3·469	0·334	3·803
100	0·0128	0·0388	0·0516	700	3·899	0·344	4·243
120	0·0419	0·0619	0·1038	800	4·2 4	0·350	4·574
140	0·0957	0·0877	0·1834	900	4·465	0·355	4·820
160	0·1758	0·114	0·2898	1000	4·653	0·358	5·011
175	0·2517	0·1333	0·3850	1100	4·797	0·360	5·157

It will be seen that the contribution from the set of discrete frequencies becomes negligible at temperatures below 60° Abs. At and below that temperature, the residual spectrum of frequencies alone is responsible for the entire heat capacity of the crystal. At higher temperatures, however, the contribution of the spectrum of discrete frequencies rapidly increases and ultimately becomes responsible for all except 1/16th part of the specific heat.

In order to exhibit the over-all success of the theory in explaining the thermal behaviour of diamond, the figures for the atomic heat shown in Table I have been plotted as a curve (Fig. 2) on a scale which is adequate

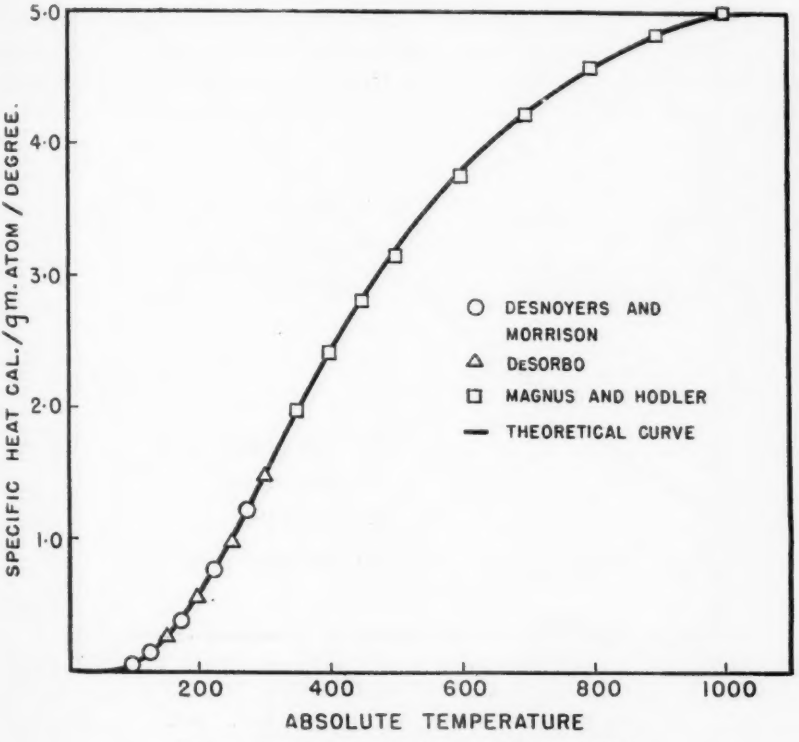

FIG. 2. Specific Heat of Diamond from 0 to 1000°.

to represent the data except in the region where it runs nearly parallel to the axis of temperature. In the temperature range between 300 and 1000° K., the values determined by Magnus and Hodler have been used, while in the

lower ranges, the data of DeSorbo as well as those reported by Desnoyers and Morrison have been put in. It will be seen that no deviations between theory and experiment which are at all significant are noticeable on the scale of the graph.

For temperatures below 300°, the determinations by Pitzer, DeSorbo and by Desnoyers and Morrison are available, but since the two latter sets of determinations are in good agreement, they have been plotted in a graph covering the temperature range between 160 and 300° K. (Fig. 3). The

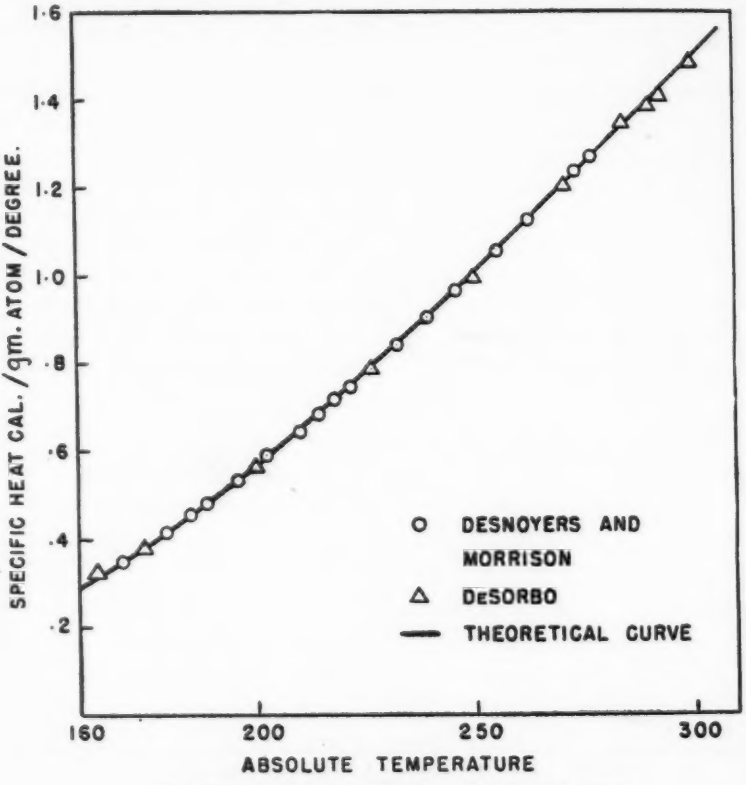

FIG. 3. Specific Heat of Diamond from 160 to 300°.

scale on which this figure has been drawn is adequate to disclose any systematic deviations between theory and experiment, had such existed. No such deviations are noticeable and hence it is evident that throughout the range of temperature in which the spectrum of discrete frequencies is principally

responsible for the heat capacity of diamond (160 to 1000° K.), the theory is in very satisfactory accord with the facts.

We shall next consider the very lowest temperatures where the value of C_p retreats into the third or fourth decimal place. The theoretical curve for this region has been drawn in Fig. 4, an adequately large scale being used for the ordinates, and the data reported by DeSorbo and by Desnoyers and Morrison have been plotted alongside of it. At the lowest temperatures the values of DeSorbo exhibit a distinct scatter, many of them lying above the theoretical curve. On the other hand, the more recent data of Desnoyers and Morrison lie smoothly on the curve up to 50°. The agreement between theory and experiment in this range made apparent by the graph must be considered highly satisfactory.

In the temperature range between 50° and 60° K., the experimental values plotted in Fig. 4 lie above the theoretical curve, the magnitude of the differences being a few units in the fourth place of decimals. From Fig. 5 which

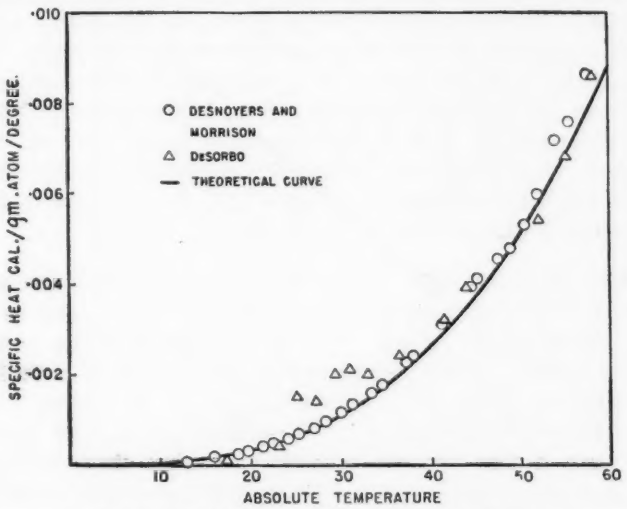

FIG. 4. Specific Heat of Diamond from 0 to 60°.

represents a comparison between theory and experiment in the range between 60 and 160° K. it will be seen that such differences become distinctly more pronounced at higher temperatures, reaching a maximum value of 0·007 at about 100°; they steadily diminish again at higher temperatures and finally cease to be noticeable on the graphs beyond 150° K. Since the value of the specific heat at 100° K. is itself very low, being only 0·059, the difference

between theory and experiment expressed as a percentage of the specific heat is 12%, but to express the difference in this way exaggerates its significance. Since, however, the discrepancy is real, we shall consider and comment upon its origin.

4. SPECTROSCOPIC BEHAVIOUR OF NON-IDEAL DIAMONDS

An explanation of the differences which are noticeable between theory and observation in the values of C_p in the range between 50 and 150° K. is not far to seek. The theoretical calculations refer to the case of an ideal crystal. They could therefore be expected to show a complete agreement with the experimentally determined specific heats if only the latter had also been made with ideal diamonds. Actually, however, determinations of specific heat require fairly large masses of material and it is therefore inevitable that they are made with diamonds of an inferior sort. It may be noted that DeSorbo used 80 grams of fragmented bort. He noticed that some of the crystals exhibited colour and also that about 20% of the material was fluorescent. Desnoyers and Morrison report that the sample used by them consisted approximately of 160 grams of industrial diamonds, their average dimensions being about 3 mm. They also remark that most of their diamonds were lightly coloured, either yellow, brown or green but that none contained occlusions. It is evident from these descriptions that we are concerned here with the class of diamond that exhibits its non-ideality of crystal structure in a visible manner, in other words, shows colour in daylight and luminescence under ultra-violet illumination.

The spectroscopic behaviour of diamonds of all sorts has been investigated by a variety of methods over a period of many years by the author and his collaborators. It will suffice here to refer to the results reported in a paper by Miss Anna Mani[3] recording a detailed study of the fluorescence and absorption spectra of twenty-two diamonds of various sorts. When the crystals are cooled down to liquid air temperature, these spectra sharpen notably, and it then becomes possible to analyse them in detail. Intercomparison of the fluorescence and absorption spectra enables the frequencies representing electronic transitions to be identified and distinguished from those due to the vibrational transitions appearing in combination with them. The result emerges clearly that the spectroscopic behaviour of diamonds which are colourless as seen by daylight and of those which exhibit various shades of brown, yellow or green is strikingly different. Diamonds of the former sort exhibit a blue fluorescence and the atomic vibration spectrum deduced from studies thereof is generally similar to that shown in the chart

reproduced above as Fig. 1 in the text. On the other hand, diamonds exhibiting visible tints by daylight fluoresce with a greenish yellow colour, the analysis of the spectrum of which discloses many features both in the electronic and atomic vibration spectra which are absent in the blue luminescence of

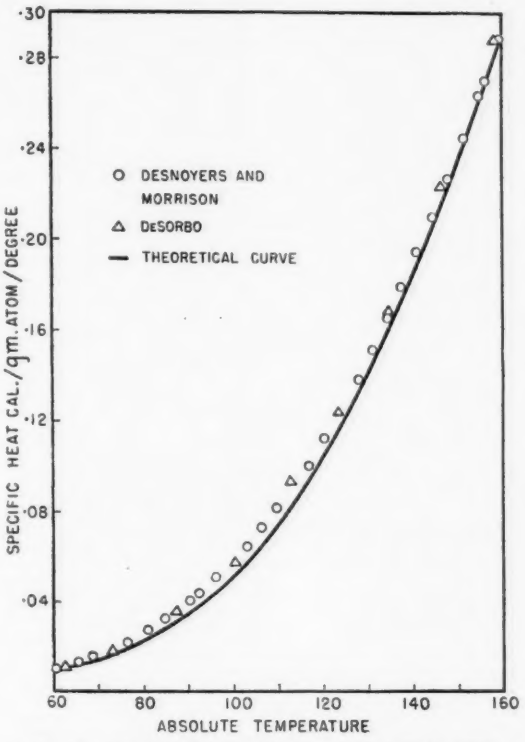

FIG. 5. Specific Heat of Diamond from 60 to 160°.

colourless diamonds. The most prominent of the additional features in the vibration spectrum is a band stretching from 257 to 443 cm.$^{-1}$ with its peak at 359 cm.$^{-1}$

It is clear from the facts recited above that the atomic vibration spectrum of non-ideal diamonds differs notably from that of the ideal material. The difference arises chiefly in the region of the residual spectrum of frequencies and may be described as an enhancement of its strength in the region of frequencies about 359 cm.$^{-1}$ Since the total number of atomic degrees of freedom is invariant, such enhancement would necessarily involve a diminu-

tion in the strength of the residual spectrum at higher frequencies between 359 cm.$^{-1}$ and the upper limit of 621 cm.$^{-1}$ A change in the character of the residual spectrum of the nature indicated would evidently result in altering the specific heat of the crystal. The Einstein function for a frequency of 359 cm.$^{-1}$ has a negligible value at temperatures below 50° K. It increases most rapidly in the temperature range in the vicinity of 100°, and at higher temperatures tends more slowly towards its limiting value. The change in the character of the residual spectrum would thus result in an increase of the specific heat of non-ideal diamonds which would be vanishingly small at very low and at very high temperatures and would be most prominent at about 100° K. This describes what is actually observed.

ACKNOWLEDGEMENT

The author much appreciates the courtesy of Messrs. Desnoyers and Morrison in having made the results of their valuable new determinations available to him in advance of publication.

SUMMARY

The evaluation of the heat capacity of diamond on the basis of the theory of specific heats advanced by the author is discussed and the results are compared graphically with the latest available experimental data. A striking over-all agreement emerges over the whole of the temperature range between 0 to 1000° K. The experimental values are however slightly in excess of the theoretical ones in the limited range between 50 and 150° K., the difference in the value of C_p being a maximum of 0·007 at about 100° K. and ceasing to be noticeable both below 50° K. and above 150° K. This small excess is explained as a consequence of the use in the experimental determinations of industrial diamonds whose spectroscopic behaviour is observably different from that of the ideal material.

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DISTRIBUTION OF RADIOACTIVITY IN THE ROCKS OF SOUTH INDIA

Part IV. Fluorine-Bearing Granites of Podili–Kanigiri Area and Associated Rocks

By C. Mahadevan, F.A.Sc. and A. V. R. Sastry
(Department of Geology, Andhra University, Waltair)

Received August 23, 1957

An interesting group of rocks in the Podili–Kanigiri area and their extension were reported to have characteristic features suggesting regional granitisation of pre-existing schistose formations. Fluorine was often detected in these rock types and the area occupied by these granitised rocks has earned a notoriety due to the prevalence of endemic fluorosis (Raghavachari *et al.*, 1940). A systematic study of this region has been in progress during the last 6 years by the scholars of the Geology Department under one of us (C. M.). Successive stages of feldspathisation of the schists into what appear to be true granites can be easily traced in the field. The most interesting fact about these granites is that no one outcrop looks like any other; while from the mineral assemblage and texture they could be described as granites there is wide variation in the accessories even within short distances. In some, streaks and lenses of fluorite with azure-blue colour, are characteristic. There are also disseminations of arsenopyrites, muscovite mica, calcite and epidote occurring in different proportions. Most of the feldspar is pink orthoclase. Sometimes blue quartz, pyrites, rhombic pyroxene and microcline constitute the rock and the rocks have a dark colour. Almost complete granitisation of the schistose formations with palimpsest structures are frequently noted. All the evidences so far found support the surmise that the intrusion of granites was intimately involved with the processes of sericitisation, silicification and feldspathisation, all constituting different facets of the same process. The intrusion of granites seems to have been followed by pneumatolytic and hydrothermal stages as shown by the presence of fluorite and topaz.

Mahadevan and Aswathanarayana (1953) and Aswathanarayana (1954) from studies on the radioactivity of charnockites suggested that metasomatically formed charnockites show greater radioactivity than magmatic types. The Podili granites offer an excellent test material for the confirmation or otherwise of our earlier ideas in work, more particularly because of the opportunity of comparing these results with the radioactivity of normal granites which occur not too far from here.

Methods of Study.—Twenty-seven representative specimens from Podili-Kanigiri area and Bellamkonda area were taken for the determination of β-activity. The experimental technique of the determination of radioactivity of rocks is the same, as was described by Aswathanarayana (1954), except that all the sample is made to pass through 40 mesh and is taken for the measurement. The β-activity of 27 rock specimens of granites and associated rocks was determined. The data and a summarised description pertaining to the specimens are presented in Table I.

The data on the chemical analysis (for 11 rocks) and modal composition (for 16 rocks), which were carried out by the research scholars of the Department, are shown in Tables II and III.

DISCUSSION

The distribution of radioactivity in the granites and associated rocks is studied in relation to the (i) chemical constitution, (ii) mineralogical constitution, and (iii) petrogenesis.

(*i*) *Radioactivity and chemical constitution*.—The relationship between the radioactivity and the percentage of SiO_2 and Fe-, Mg-, Ca-oxides (in granites and feldspathised schists) is represented in Figs. 1 and 2 respectively. It can be seen from Table II, and Fig. 1, that the radioactivity increases with increase in the SiO_2 content in the case of granites. The rapid increase in the radioactivity of the Kanigiri granites without proportional increase in SiO_2 content may be due to the presence of small inclusions of uranium and/or thorium-bearing minerals formed during the injection of granitic juices known as 'ichors' into the pre-existing rocks.

In the case of feldspathised schists radioactivity increases with the increase in the total content of Fe-, Mg-, Ca-oxides. In this connection it may be stated that when the desilication change is wholly or largely one of basification (introduction of Fe, Mg, Ca) it is characterised by increase, commonly attaining geochemical culmination of one or more, of the minor constituents TiO_2, P_2O_5 and MnO (Reynolds, 1946). It has to be understood that even though the increase in radioactivity of these feldspathised schists apparently corresponds to the increase in the total content of Fe-, Mg-, Ca-oxides the increase in radioactivity may be due to the increase in minor constituents containing uranium and thorium.

(*ii*) *Radioactivity and mineralogical constitution*.—It can be seen from Table III that the radioactivity increases with quartz content as well as with plagioclase feldspar content in the case of granites. The radioactivity of the feldspathised schists appears to increase with the increase in the biotite

TABLE I

TABLE I

S. No.	Specimen	Description	Sheet No. and locality	Radioactivity ($\times 10^{-6}$ gm. of e.U./gm. of rock)
1	2	3	4	5
	GRANITES			
1	Pink granite	Per., Qz., Or., Di., and Bi., Mt., Gar., Tpz., Ru.	57 M/14, 472′ hill near Errapalem	45·86
2	Coarse-grained granite	Or., Qz., Pl., Bi., Hor. and Mt., Sp., Ap., Zr., Tpz.	57 M/7, Western fringes of Kanigiri Hill	40·15
3	Fine-grained granite	Or., Qz., Pl., Bi., Hor. and Mt., Zr., Ap., Tpz.	-do-	38·85
4	Fluorine-bearing granite	Qz., Or., Pl., Bi. and Fl., Tpz., Ap., Zr.	-do-	37·51
5	Basic segregation in granite	..	-do-	33·63
6	Fluorine-bearing granite	..	57 M/10, 3 furlongs N.-E. of Podili village	24·96
7	Garnetiferous granite gneiss	Or., Qz., Per., Pl. and Hy., Mt., Tpz.	57 M/14, Illapavarulu Hills	16·82
8	Granitic rock	Qz., Fel., Bi. and Acc.	57 M/6, from 1123′ hillock	13·84
	FELDSPATHISED SCHISTS AND GNEISSES			
9	Feldspathised biotite schist	Bi., Qz., Fel. and Acc.	57 M/6, from 759′ hillock	29·89
10	Feldspathised biotite schist	Per., Bi., Pl., Qz., Mt. and Tpz., Zr., Ap.	57 M/14, West of Uppalapadu	23·64
11	Feldspathised schist	Pl., Bi., Qz., Chl., Mt. and Ap., Zr.	57 M/7, Western fringes of Kanigiri Hill	22·85
12	Feldspathised schist	Per., Or., Pl., Hor., Qz. and Mt., Tpz., Zr., Ap.	57 M/14, near 18th milestone on Ongole-Podili Road	16·14
13	Feldspathised gneiss	Qz., Fel., Bi. and Acc.	57 M/6, from Selanutala	12·86
14	Silicified schist	Fel., Qz., Bi., Chl. and Acc.	57 M/6, from Chinmanagundam	5·20

TABLE I (*Contd.*)

S. No.	Specimen	Description	Sheet No. and locality	Radioactivity ($\times 10^{-6}$ gm. of e.U./gm. of rock)
1	2	3	4	5
	SCHISTS			
15	Mica Schist	Bi., Chl., Qz. and Acc.	57 M/6, from 1047 hillock	28·98
16	Chlorite schist	Chl., Qz., Ser., Bi. and Acc.	57 M/6, from Ganikonda	21·02
17	Fine-grained biotite hornblende schist	Per., Or., Pl., Bi., Hor., Qz., Mt. and Tpz., Ap.	57 M/14, 1 mile N.-E. of 18th milestone on the Ongole-Podili Road	14·72
	BATHOLITHIC (?) GRANITES			
18	Epidote granite	Or., Qz., Per., Ep., Pl. and Hor., Bi., Chl., Zoi., Mt., Ap.	65 D/2, from Bellamkonda Hill	15·04
19	Pink granite	Per., Qz., Or., Pl. and Hor., Bi., Chl., Mt.	65 D/2, ½ mile N.-E. of Gorantla	14·74
20	Fine-grained granite	Per., Qz., Mi., Or., Pl., Bi. and Ap.	65 D/2, 2 furlongs N.-E. of Gorantla	12·99
21	Quartzose granite	Qz., Per., Or., Pl. Mi.	65 D/2 Near Ninducherla	11·63
	PHYLLITES AND SLATES			
22	Slate	(Chl., Bi., Qz. and Acc.)	57 M/6, from hills in the North-Western extremity of the sheet	25·92
23	Garnetiferous phyllitic slate	(Chl., Bi., Qz., Gar. and Acc.)	57 M/6, near Tadivaripalle	24·97
24	Phyllitic slate	(Chl., Bi., Qz. and Acc.)	57 M/6, near Nagellamudupu	24·33
25	Phyllite	..	57 M/6, from a well near Bachchalakurapadu	21·43
26	Phyllitic slate	(Chl., Bi., Qz. and Acc.)	57 M/6, near Tadivaripalle	21·22
27	Phyllite	(Chl., Bi., Qz. and Acc.)	57 M/6, near Ummareddipalle	21·05

LEGEND

Qz. .. Quartz	Fel. .. Feldspar	Ru .. Rutile
Per. .. Perthite	Hy. .. Hypersthene	Ser. .. Sericite
Or. .. Orthoclase	Gar. .. Garnet	Tpz. .. Topaz
Mi. .. Microcline	Zoi. .. Zoisite	Ap. .. Apatite
Bi. .. Biotite	Ep. .. Epidote	Zr. .. Zircon
Hor. .. Hornblende	Chl. .. Chlorite	Fl. .. Fluorite

TABLE II. *Chemical analysis of granites, schists and gneisses*

Qz.	..	Quartz	Hy.	..	Hypersthene	Ser.	..	Sericite			
Per.	..	Perthite	Gar.	..	Garnet	Tpz.	..	Topaz			
Or.	..	Orthoclase	Zoi.	..	Zoisite	Ap.	..	Apatite			
Mi.	..	Microcline	Ep.	..	Epidote	Zr.	..	Zircon			
Bi.	..	Biotite	Chl.	..	Chlorite	Fl.	..	Fluorite			
Hor.	..	Hornblende									

TABLE II. *Chemical analysis of granites, schists and gneisses*

Chemical constituent	Specimen numbers										
	1	2	4	7	19	20	9	10	12	17	13
SiO_2	75·33	74·66	76·00	72·92	71·05	65·90	61·96	55·80	62·42	54·82	79·41
Al_2O_3 ..	12·93	12·21	10·46	14·51	15·13	15·04	7·85	14·20	16·50	12·91	7·50
Fe_2O_3 ..	0·30	1·46	1·69	0·35	0·44	0·96	7·30	6·08	1·64	5·08	1·10
FeO ..	0·95	2·66	2·50	0·34	1·93	4·95	16·25	8·48	3·50	10·40	3·46
MgO ..	0·20	0·33	0·26	0·08	0·48	1·09	2·30	1·28	2·76	7·20	0·56
CaO ..	0·40	0·76	2·02	0·91	1·50	2·67	1·60	1·48	2·25	4·40	1·90
Na_2O ..	2·98	1·22	1·52	2·40	3·14	2·95	0·70	0·70	1·01	1·60	1·25
K_2O ..	6·30	6·36	4·56	8·20	5·25	6·12	1·90	11·90	12·90	3·40	3·20
P_2O_5 ..	0·10	..	0·28	..	..	..	..	..	..	0·20	..
MnO ..	0·09	..	..	..	..	..	..	..	..	..	..
TiO_2 ..	0·11	0·14	0·17	0·11	0·05	0·56	0·15	0·20	0·15	0·10	..
H_2O ..	N.D.	0·40	N.D.	N.D.	0·61	0·45	0·58	N.D.	N.D.	N.D.	1·58
F ..	..	..	0·039	..	..	..	..	N.D.	N.D.	N.D.	..
TOTAL ..	99·69	100·20	99·50	99·82	99·58	100·69	100·49	100·02	101·13	100·17	99·96

N.D. = Not determined.

Specimen Nos.	..	1 and 7	Analyst:	M. Krishna Murthy	.. 1954
,, ,,		2 and 4	,,	C. Bhimeswara Rao	.. 1956
,, ,,		19 and 20	,,	S. Subba Rao	.. 1956
,, ,,		9 and 13	,,	M. Ranga Rao	.. 1956
,, ,,		10, 12, and 17	,,	C. V. S. Sastry	.. 1954

TABLE III

Modal composition of granites, schists and gneisses

Sp. No.	Specimen	Quartz	Potash feldspar	Plagio-clase	Perthite	Biotite and/or (chlorite)	Horn-blende and/or (epidote)	Accessories
	GRANITES							
1	Pink granite	33·05	33·05	..	42·07	1·15	..	2·22
2	Coarse-grained biotite granite	37·51	18·51	13·42	29·81	8·14	..	2·52
3	Fine-grained granite	31·71	37·04	..	20·93	8·20	1·20	0·94
4	Fluorine-bearing granites	40·33	36·15	12·20	..	8·68	..	2·68
7	Garnetiferous granite gneiss	24·52	57·30	4·76	12·53	..	..	0·06
18	Epidote granite	35·10	39·15	2·71	15·64	..	(6·39)	1·32
19	Pink granite	28·02	13·80	2·22	48·68	..	..	7·28
20	Fine-grained granite	17·10	25·22	5·08	40·21	..	..	Biotite and accessories: 12·39
21	Quartzose granite	49·04	14·41	5·75	30·77	..	..	..
	SCHISTS AND GNEISSES							
9	Feldspathised biotite	34·27	14·08	5·78	..	36·46	..	Mt.: 9·4
10	Feldspathised schist	..	..	9·4	66·00	16·20	..	Mt.: 8·64
11	do.	9·41	..	69·34	..	15·38	..	4·82
12	do.	3·42	13·00	10·40	62·03	9·84		2·54
17	Fine-grained biotite hornblende schist		50·20			42·10		7·40
13	Feldspathised gneiss	58·72	27·53		..	11·91	..	1·81
14	Silicified schist	40·72	46·75		..	12·10	..	0·41

Specimen Nos. .. 1 and 7 — Analyst: .. M. Krishna Murthy .. 1954
" " 2, 3, 4 and 11 — " C. Bhimeswara Rao .. 1956
" " 18–21 — " S. Subba Rao .. 1956
" " 9, 13 and 14 — " M. Ranga Rao .. 1956
" " 10, 12 and 17 — " [illegible] .. 1956

content. Perhaps topaz, zircon and apatite which occur as inclusions in biotite may increase the radioactivity of these rocks.

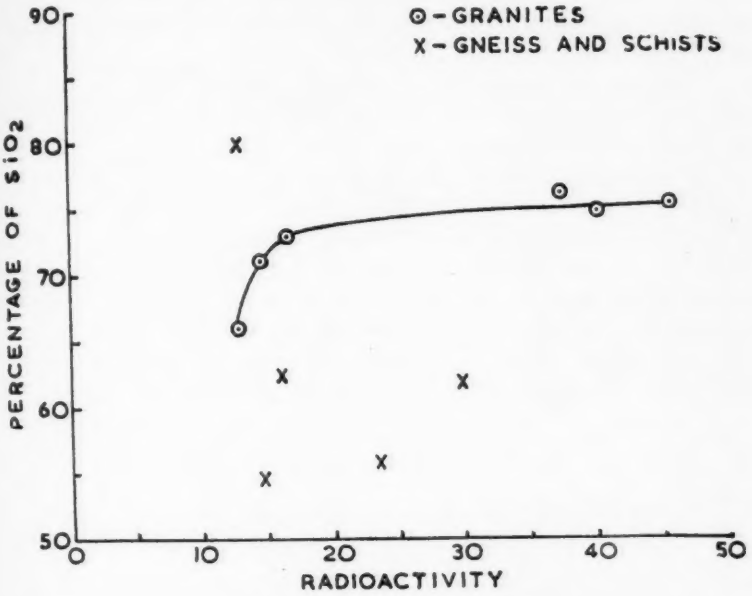

FIG. 1. Relationship between the Percentage of SiO_2 and Radioactivity of Granites and Feldspathised Schists.

Specimen Nos. .. 1 and 7 Analyst: .. M. Krishna Murthy .. 1954
" " 2, 3, 4 and 11 " C. Bhimeswara Rao .. 1956
" " 5, 6 and 8 " S. Sibba Rao .. 1956
" " 9, 13 and 14 " [illegible] .. 1956
" " 10, 12 and 15 " [illegible] .. 1956

(*iii*) *Radioactivity and Petrogenesis.*—Systematic work by the research scholars in the Geology Department, Andhra University, has proved that the Kanigiri–Podili granites, which are fluorine-bearing, have been formed by the replacement of pre-existing rocks by granitic juice or 'ichor'. The volatiles have played a dominant role in the formations of these granites. In confirmity with our previous observations of the increased radioactivity in the case of metasomatically formed charnockites (Mahadevan *et al.*, 1953; Aswathanarayana, 1954), we find here a similar observation. The Bellamkonda granites on the other hand appear to be the normal batholithic type and have lower radioactivity content ($13{\cdot}6\times10^{-6}$ gm. of e.U./gm. of rock) as compared with the Kanigiri–Podili granites ($31{\cdot}45\times10^{-6}$ e.U./gm. of rock).

By the difference in degree of assimilation of the pre-existing rocks by the intruding magma, various types of rocks may be formed resulting in the

wide variation in the radioactivity of these rocks. In this connection it may be stated that the radioactivity of granites and feldspathised schists depend upon the content of the radioactive matter in (i) the pre-existing rocks, (ii) the intruding magma and (iii) also on the extent of intermingling of the

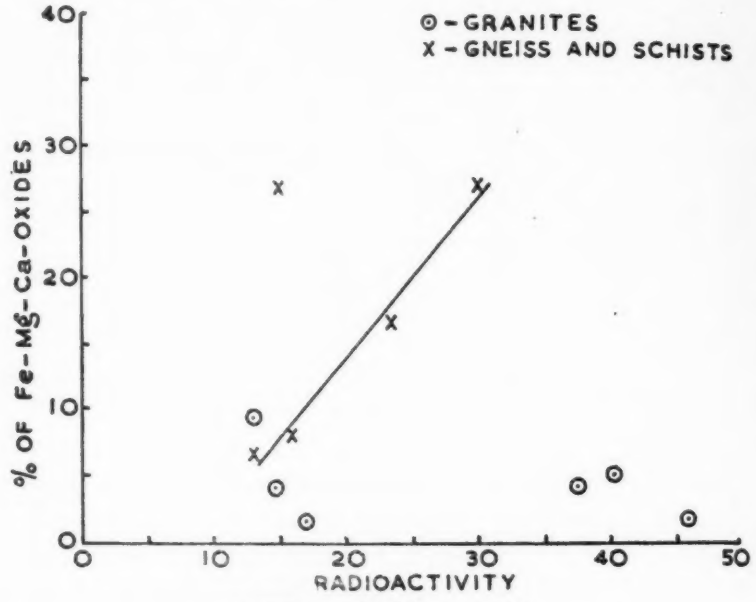

FIG. 2. Relationship between the Percentage of Fe, Mg, Ca Oxides and Radioactivity of Granites and Feldspathised Schists

two. In the field, as has been said earlier, the schistose formations grade into feldspathised schists and further into what appears to be true granites. To study the affects of feldspathisation on the country rocks, specimen Nos. 17, 12 and 10 have been chosen. Specimen No. 17 represents fine-grained biotite hornblende schist while specimen Nos. 12 and 10 represent feldspathised schist and intensely feldspathised schist respectively. The radioactivity content of the fine-grained biotite hornblende schist ($14{\cdot}72\times10^{-6}$ e.U./gm. of rock) is very low when compared to other schists (Nos. 15 and 16—$28{\cdot}98\times10^{-6}$ and $21{\cdot}02\times10^{-6}$ gm. of e.U./gm. of rock). This is a very good example to show how the study on the distribution of radioactivity reflects on the petrogenetic history of the rock types. The low radioactivity of the biotite hornblende schist may probably be due to its origin by metamorphism of basic igneous rocks which are known to contain little or very

little of radioactive matter when compared to other types of igneous rocks. Part of its radioactive content may be due to either the effect of metamorphism of earlier basic rocks or more probably the effect of large-scale granitisation of the country rocks. It is concluded (Sastry, 1954) from Osann's diagram that the original rock metamorphosed was of igneous origin. As studied from Von Wolff's Q.L.M. diagram by plotting 17, 12 and 10, it is concluded (Sastry, 1954) that the added constituents were silica, alumina and potash whereas iron, calcium, magnesium and soda were subtracted. In Fig. 2 (showing the relationship between the total % of Fe-, Ca-, Mg-oxides and radioactivity of the feldspathised schists) specimen No. 17 (which is not a feldspathised schist) falls outside the curve. Even though there is not much difference in the radioactivity of 17 and 12 there is a great difference in the total % of Fe-, Ca-, Mg-oxides, which confirms the above surmise. From 17–12, feldspar increases and quartz decreases (desilication) indicating the feldspathised nature of 12 and 10, starting from 17. The radioactivity also increases from 14·72 (17) to 23·64 (10) with increase in feldspathisation.

Summary and Conclusions

The study on the distribution of radioactivity in granites and associated rocks, with relevant geological and chemical data confirm that:

(i) the metasomatically formed granites will have higher radioactivity than the normal batholithic type of granites,

(ii) granitisation will enhance the radioactivity of the country rocks, and

(iii) radioactivity increases with the increase in the feldspathisation of the country rocks.

The study on the distribution of radioactivity in rocks will be of great use in suggesting the petrogenetic history of the rocks.

Acknowledgements

The authors are thankful to Dr. U. Aswathanarayana for his keen interest during the progress of these investigations. Our thanks are due to Messrs. M. Krishna Murthy, C. Bhimeswara Rao, C. V. S. Sastry, M. Ranga Rao and S. Subba Rao, who have kindly spared some of their specimens for this work. The financial assistance of the Council of Scientific and Industrial Research is thankfully acknowledged.

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A SYNTHESIS OF STILLOPSIDIN AND ITS METHYL ETHERS*

By K. R. Laumas, S. Neelakantan and T. R. Seshadri, F.A.Sc.
(*Department of Chemistry, University of Delhi, Delhi-8*)

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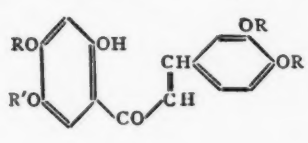
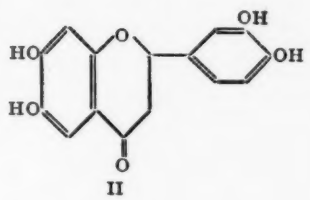
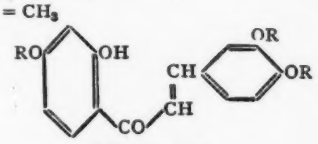
Seikel and Geissman[1] isolated a chalkone hexoside, stillopsin, from the flowers of *Coreopsis stillmanii*. They showed that it was a glucoside of 2 : 4 : 5 : 3′ : 4′-pentahydroxychalkone (I, stillopsidin). Later, King *et al.*[2] obtained the same chalkone from the heartwood of *Plathymenia reticulata* in which it was accompanied by the corresponding flavanone which was called plathymenin (II). Obviously, partial flavanone conversion had taken place in the heartwood. In view of the fact that other Coreopsis species contain glycosides of butein (III), it could be suggested that the evolution of stillopsidin involves an extra stage of oxidation leading to the introduction of a hydroxyl group in the 5-position. Stillopsidin, therefore, is 5-hydroxybutein. Following this concept, it should be possible to oxidise butein to stillopsidin. Using butein trimethyl ether (III *a*), nuclear oxidation could now be conveniently carried out by means of alkaline persulphate to produce stillopsidin trimethyl ether (I *a*) which when partially methylated yields the known compound, stillopsidin tetramethyl ether (I *b*).



I R = R′ = H
I*a* R = CH_3; R′ = H
I*b* R = R′ = CH_3



II



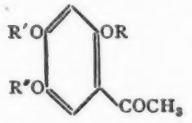
III R = H
III*a* R = CH_3

The free pentahydroxychalkone (stillopsidin) itself could not be obtained by demethylation of the above methyl ether because it was accompanied by

* The work discussed in this paper was completed in the 1954–55 session and was embodied in a thesis. In view of the publication of Seikel *et al.*,[3] only matter not found in their paper is presented here.

complex changes. Hence, direct synthesis had to be carried out. Seikel *et al.*[3] achieved this synthesis in rather poor yields by carrying out the chalkone condensation with 2:4:5-trihydroxyacetophenone and protocatechuic aldehyde in the presence of alkali. A more convenient method is to use the benzoates of the two components, effect the condensation in the presence of hydrogen chloride and finally remove the benzoyl groups. This gives rise to an easily purified product in a much better yield. Further conversion into the flavanone to obtain plathymenin has been already reported by Seikel *et al.*[3]

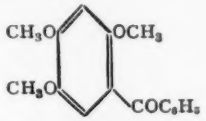
In the course of the abovementioned work, 2:5-dihydroxy-4-methoxyacetophenone (IV) and 2-hydroxy-4:5-dimethoxyacetophenone (V) were prepared as intermediates. The former was obtained from pæonol by oxidation with alkaline potassium persulphate[4] and its properties agreed very closely with those of the substance prepared by Bargellini and Aureli[5] by the demethylation of 2:4:5-trimethoxyacetophenone (VI). However, they considered this demethylation product to be 2:4-dihydroxy-5-methoxyacetophenone (VII). In view of the fact that a methoxyl group located para to a carbonyl is more resistant to demethylation than those in the meta and ortho positions, it appeared possible that the sample obtained by Bargellini and Aureli[5] was really the 4-methyl ether. This has been confirmed by the demethylation of 2-hydroxy-4:5-dimethoxyacetophenone (V) with hydrobromic acid whereby the product was found to be identical with the one obtained by nuclear oxidation of pæonol. Further, the 5-methyl ether (VII) has also been prepared by employing the 4-benzyl ether of resacetophenone and subjecting it to nuclear oxidation, partial methylation and debenzylation.



IV $R = R'' = H$; $R' = CH_3$
V $R = H$; $R' = R'' = CH_3$
VI $R = R' = R'' = CH_3$
VII $R = R' = H$; $R'' = CH_3$

A similar error seems to exist in the work of Bargellini and Martegiani[6] when they considered that the partial demethylation of 2:4:5-trimethoxybenzophenone (VIII) yielded the corresponding 5-monomethyl ether. Here also, the substance is found to agree in its properties with the 4-methyl ether obtained by the nuclear oxidation of 2-hydroxy-4-methoxybenzophenone. As relevant to the above discussion, it may be mentioned that Gardner *et al.*[7]

have recently found that partial demethylation of 2:3:4-trimethoxyacetophenone yields the 4-monomethyl ether and not the 3-monomethyl ether as originally thought by Baker *et al.*[8]



VIII

Experimental

2:5-*Dihydroxy*-4:3′:4′-*trimethoxychalkone* (*I* a).—To a stirred solution of 2-hydroxy-4:3′:4′-trimethoxychalkone[9] (butein trimethyl ether) (2 g.) in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (2 g. in 16 c.c. of water) was added dropwise a solution of potassium persulphate (2 g. in 50 c.c. of water) in the course of 2 hours (18–20°). The mixture was allowed to stand for 24 hours, and neutralised with concentrated hydrochloric acid (Congo red). The precipitated unreacted chalkone was filtered off and the filtrate extracted with ether three times. The aqueous solution was treated with sodium sulphite (6 g.) and concentrated hydrochloric acid (40 c.c.) and heated on a boiling water-bath for ½ hour, when an orange-yellow solid separated. After keeping overnight in the refrigerator, it was filtered and washed with a little cold water. On crystallisation from methyl alcohol, the dihydroxychalkone was obtained as deep orange-yellow prisms, m.p. 204–05°. Yield, 0·4 g. (Found: C, 65·5; H, 5·5; $C_{18}H_{18}O_6$ requires C, 65·5 and H, 5·5%). It gave an evanescent green colour with alcoholic ferric chloride and a pink colour with aqueous sodium hydroxide.

2-*Hydroxy*-4:5:3′:4′-*tetramethoxychalkone* (*stillopsidin tetramethyl ether*) (*I* b).—A solution of the above chalkone (I *a*) (1 g.) in dry benzene (40 c.c.) and dry acetone (40 c.c.) was refluxed with dimethyl sulphate (0·35 c.c., 1·1 mole) and anhydrous potassium carbonate (2 g.) for 6 hours, and filtered. The chalkone, obtained after distilling off the solvent from the filtrate, crystallised from alcohol as orange-yellow plates, m.p. 173–74°. Yield, 0·7 g. It gave a brown colour with alcoholic ferric chloride (*see* Seikel and Geissman[1] and King *et al.*[2]). For comparison, this tetramethyl ether was prepared by the condensation of 2-hydroxy-4:5-dimethoxyacetophenone and varatraldehyde in the presence of caustic alkali in the cold (48 hours) whereby good yields were obtained and the substance was identical with the compound prepared by Seikel and Geissman.[1]

2:4:5-*Trihydroxyacetophenone*.—Seikel *et al.*[3] reported that the nuclear oxidation of resacetophenone does not proceed satisfactorily. By adopting

the conditions mentioned below, fairly good yields of 2:4:5-trihydroxyacetophenone could be obtained.

To a stirred solution of resacetophenone (15 g.) in potassium hydroxide (30 g. in 100 c.c. of water) was added dropwise a saturated aqueous solution of potassium persulphate (30 g.) during 5 hours and the mixture was left at room temperature for 48 hours. It was worked up as usual and the aqueous solution after hydrolysis was thoroughly extracted with ether (10 × 300 c.c.). The ether extract was evaporated to dryness and the solid washed with a small quantity of ether. It was crystallised from ether; m.p. 202–04°. Yield, 5 g.

The tribenzoate of the above acetophenone was prepared using benzoyl chloride and pyridine; m.p. 138–39°.

2:4:5:3′:4′-*Pentahydroxychalkone* (*stillopsidin*) (*I*).—A solution of 2:4:5-tribenzoyloxyacetophenone (4·8 g.) and protocatechuic aldehyde dibenzoate (3·4 g.) in dry ethyl acetate (60 c.c.) was saturated with dry hydrogen chloride for 4 hours, and left overnight. The solvent was removed under reduced pressure and the clear red syrup was boiled with alcohol (50 c.c.), cooled and decanted off. The crude chalkone benzoate was dissolved in boiling alcohol (150 c.c.) and potassium hydroxide (14 g. in 100 c.c. of water) added dropwise along with a small amount of sodium sulphite. After keeping for 4 hours, it was just acidified and the alcohol distilled off. The dark red solution was cooled in ice and the solid product collected. Extraction of the filtrate, after saturation with sodium chloride, yielded a further quantity of the hydroxychalkone. It was freed from benzoic acid by repeatedly washing with hot benzene and finally crystallised from aqueous methyl alcohol yielding orange plates; m.p. 226–28°. Yield, 0·7 g. (Found: C, 62·1; H, 4·1; $C_{15}H_{12}O_6$ requires C, 62·5 and H, 4·2%). It gave a dark brown colour with alcoholic ferric chloride (*see* Seikel and Geissman[1] and King *et al.*[2]).

Partial demethylation of 2-*hydroxy*-4 : 5-*dimethoxyacetophenone*.—2-Hydroxy-4:5-dimethoxyacetophenone (0·5 g.) was dissolved in acetic acid (10 c.c.) and hydrobromic acid (constant boiling; 10 c.c.) added. The solution was refluxed gently for 2 hours, and then diluted with water. Most of the acid was neutralised by the addition of sodium bicarbonate and the mixture extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and distilled when a brown oil was obtained which solidified on keeping in the refrigerator. It crystallised from water as pale brown, elongated rods; m.p. 164–65°. It gave an evanescent green colour with alcoholic ferric chloride. It was identical with 2:5-dihydroxy-4-methoxyaceto-

phenone, obtained by the persulphate oxidation of pæonol;[4] the mixed melting point was also undepressed.

2: 4-*Dihydroxy*-5-*methoxyacetophenone* (*VII*): (*a*) 2: 5-*Dihydroxy*-4-*benzyloxyacetophenone*.—2-Hydroxy-4-benzyloxyacetophenone, required for this preparation, was obtained in improved yields by a modification of the method of Gulati *et al.*[10] using 1 mole of benzyl chloride and potassium iodide. It (4·8 g.) was dissolved in a mixture of potassium hydroxide (6 g. in 50 c.c. of water) and pyridine (25 c.c.). To this solution was added dropwise a solution of potassium persulphate (6 g. in 200 c.c. of water) in the course of 4 hours, keeping the temperature of the reaction mixture below 15°. The product was worked up as usual and it crystallised from alcohol as yellow plates and prisms; m.p. 160–62°. Yield, 1·2 g. (Found: C, 69·2; H, 5·4; $C_{15}H_{14}O_4$ requires C, 69·7 and H, 5·5%). It gave a green colour with alcoholic ferric chloride.

(*b*) 2-*Hydroxy*-4-*benzyloxy*-5-*methoxyacetophenone*.—The above compound (4·2 g.) was partially methylated with dimethyl sulphate (1·8 c.c.) and potassium carbonate (4 g.) in acetone (100 c.c.) by refluxing for 6 hours. The methyl ether crystallised from alcohol as stout needles; m.p. 126° (Found: C, 70·2; H, 6·2; $C_{16}H_{16}O_4$ requires C, 70·6 and H, 5·9%). It gave a dark green colour with alcoholic ferric chloride.

(*c*) *Debenzylation*.—2-Hydroxy - 4 - benzyloxy - 5 - methoxyacetophenone (1 g.) was boiled with a mixture of concentrated hydrochloric acid (10 c.c.) and glacial acetic acid (10 c.c.) for 1 hour. On cooling the mixture, a dark product separated which was filtered and dried. It crystallised from ether (charcoal) as colourless plates and prisms; m.p. 174° (Found: C, 59·0; H, 5·6; $C_9H_{10}O_4$ requires C, 59·3 and H, 5·5%). It gave a brownish green colour with alcoholic ferric chloride.

2: 5-*Dihydroxy*-4-*methoxybenzophenone*.—2-Hydroxy-4-methoxybenzophenone, required for this synthesis, was earlier prepared by the partial methylation of 2: 4-dihydroxybenzophenone by Kostanecki and Tambor[11] as well as by the partial demethylation of 2: 4-dimethoxybenzophenone by Kaufmann *et al.*[12] Now this has been prepared by Friedel and Crafts' reaction between resorcinol dimethyl ether and benzoyl chloride in dry ether solution. It (3 g.) was dissolved in potassium hydroxide (4 g. in 30 c.c. of water) and treated with potassium persulphate (4 g. in 100 c.c. of water) during the course of 3 hours, and worked up as usual. The product crystallised from alcohol as deep yellow, thin plates; m.p. 188°. Yield, 0·7 g. (Found: C, 68·4; H, 5·3; $C_{14}H_{12}O_4$ requires C, 68·8 and H, 5·0%). It gave a green colour with alcoholic ferric chloride. (Bargellini and Martegiani[6] reported

a melting point of 183-85° for the compound obtained by the partial demethylation of 2:4:5-trimethoxybenzophenone).

The above quinol derivative on partial methylation with dimethyl sulphate (1·1 mole) and potassium carbonate in acetone solution gave 2-hydroxy-4:5-dimethoxybenzophenone, m.p. 109–10°.—Bargellini and Martegiani[6] reported a melting point of 106–07° for this compound.

SUMMARY

On the consideration that stillopsidin is 5-hydroxybutein, butein trimethyl ether has been subjected to nuclear oxidation and final methylation to yield stillopsidin tetramethyl ether. Stillopsidin has now been prepared in better yields by an improved method. The product obtained by the partial demethylation of 2:4:5-trimethoxyacetophenone is shown to be 2:5-dihydroxy-4-methoxyacetophenone which has been prepared by an unequivocal method from pæonol. Similarly an authentic sample of 2:5-dihydroxy-4-methoxybenzophenone has been prepared and shown to be the same as that obtained by the partial demethylation of 2:4:5-trimethoxybenzophenone. A synthesis of 2:4-dihydroxy-5-methoxyacetophenone has also been carried out.

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THE INTERMEDIATE LAYER OF STRATIFICATION ($F_{1\cdot5}$) BETWEEN F_1 AND F_2 AT AHMEDABAD

By K. M. Kotadia

(*Physical Research Laboratory, Ahmedabad*)

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A summary of our knowledge of the so-called $F_{1\cdot5}$ layer (intermediate between F_1 and F_2) is contained in the report of a discussion on " Solar Eclipses and the Ionosphere " held in London in August 1955. The $F_{1\cdot5}$ layer is frequently observed during solar eclipses at places where the magnetic dip is less than 20°. Japanese workers reported the occurrence of $F_{1\cdot5}$ at higher dip angles.

It is known that near the geomagnetic equator, the forenoon increase of *fo* F_2 shows a marked check at about 09 hours associated with a rapid upward movement of *hp* F_2. This is often followed by a stratification of F_2 into two separate layers. At Ahmedabad (Geom. Lat. 13°·6 N., mag. Dip. 34° N.) which is situated on a latitude near the peak of noon *fo* F_2, a stratification of this sort has been more or less regularly observed since March 1956. The phenomenon starts with a decrease in the rate of increase of *fo* F_2 and an increase in the slope of the *h'-f* record. A splitting of the *h'f* trace follows, the frequency of the lower cusp or inflexion slowly decreases and tends ultimately to merge with *fo* F_1. A sequence of hourly *h'-f* ionospheric records showing the $F_{1\cdot5}$ layer during daytime are reproduced in Plate XVIII. Some examples showing F_1, $F_{1\cdot5}$ and F_2 having distinct cusps of their critical frequencies, are also reproduced in Plate XIX. In 1954 and 1955, such stratification was observed only in a few rare instances of magnetic disturbances, or transitorily for most periods near 09 and 10 hours when the F_2 layer was greatly expanded.

The inflexion corresponding to $F_{1\cdot5}$ first appears at about 9 Mc./s. and the frequency gradually falls to 6·0 or 6·5 Mc./s. by evening. *fo* $F_{1\cdot5}$ shows no definite relation to the sun's zenith distance. Its value reaches a maximum within an hour or two of its appearance and generally before noon. After reaching the maximum, it gradually decays. The height of its base remains more or less constant at 250 km. The following remarks are based on an analysis of the daily records (Figs. 1–3). In these figures are plotted monthly median values of *fo* F_1, *fo* $F_{1\cdot5}$, *fo* F_2, *h'* F_1, *h'* $F_{1\cdot5}$, *h'* F_2 and *hp* F_2 (*i.e.*, *h'* F_2 at 0·834 *fo* F_2) for January, April 1954–57 and for July and October, 1954–56. Relative sunspot number (R) is also put in there.

January (1954–57).—In this month, the height and semi-thickness of F_2 were comparatively low in 1954–56 and a bifurcation of F_2 was not observed. In 1957, with the increase in the height and semi-thickness of F_2, $F_{1\cdot5}$ became a daily feature (Fig. 1).

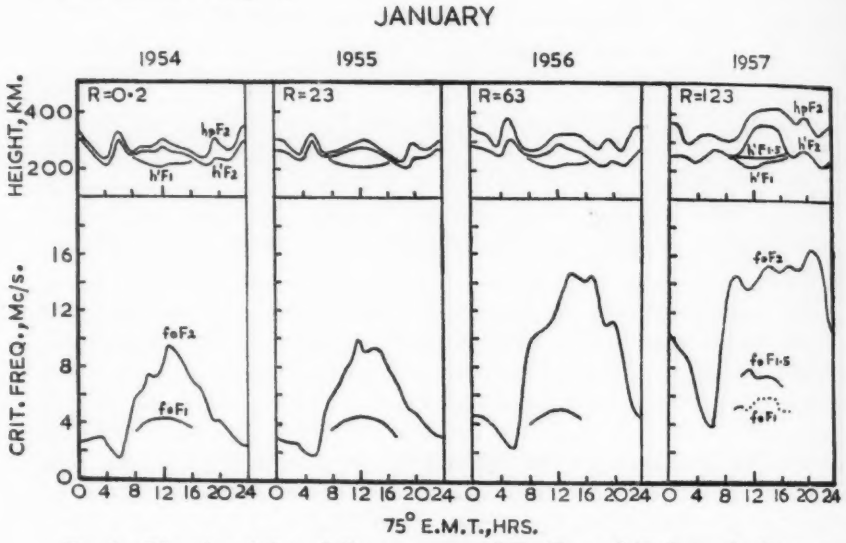


FIG. 1. Diurnal variation of the parameters of F_1, $F_{1\cdot5}$ and F_2 layers, in January 1954–57.

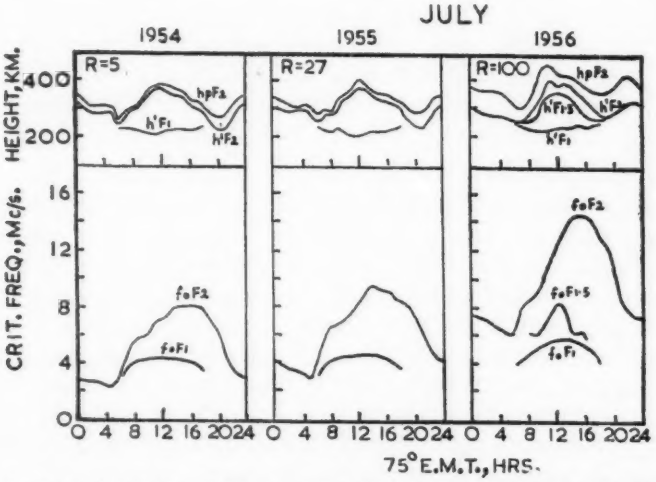


FIG. 2. Diurnal variation of the parameters of F_1, $F_{1\cdot5}$ and F_2 layers in July 1954–56.

April and October (1954–57).—In 1955, a few instances of $F_{1\cdot5}$ were observed between 09 and 10 hours.

In 1956, it became a regular daily feature (Figs. 3 *a* and 3 *b*).

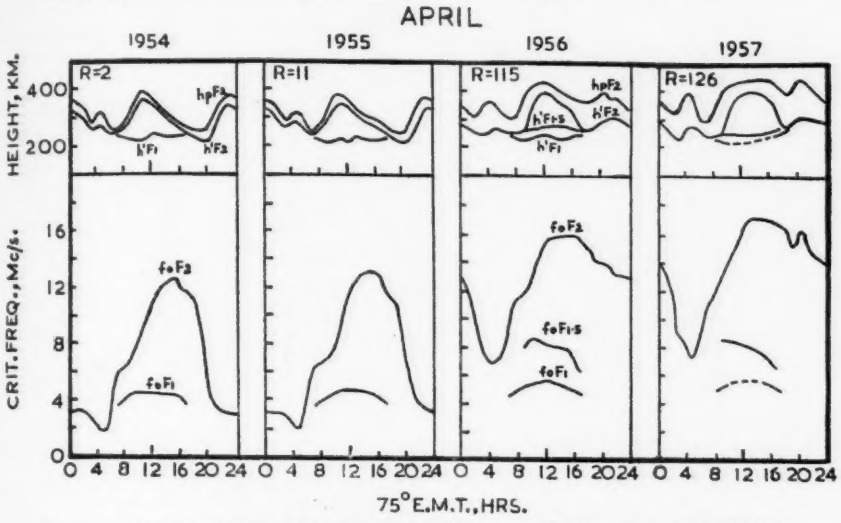


FIG. 3 *a*. Diurnal variation of the parameters of F_1, $F_{1\cdot5}$ and F_2 layers in April 1954–57.

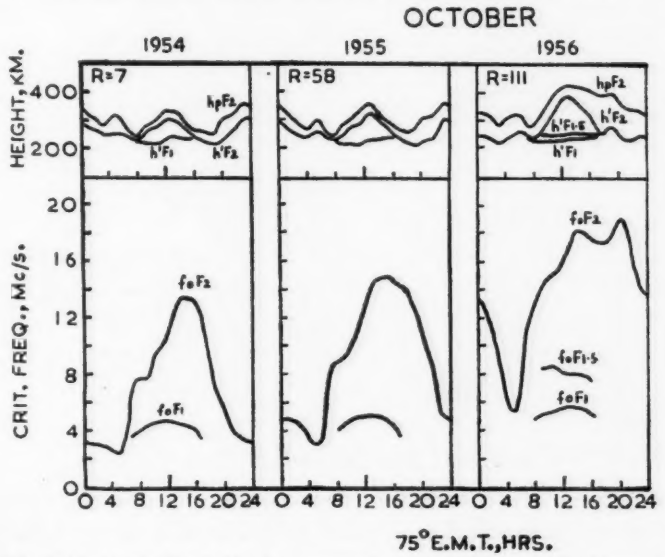


FIG. 3 *b*. Diurnal variation of the parameters of F_1, $F_{1\cdot5}$ and F_2 layers in October 1954–56.

July–Aug... (1954–56).—Even in 1954–55, a transitory and incipient stratification was frequently observed at Ahmedabad for one or two hours in the forenoon. In 1956, the phenomenon was very clear and the $F_{1\cdot5}$ remained till 14–15 hours. The $F_{1\cdot5}$ and F_2 were clearly separated. The disappearance of $F_{1\cdot5}$ was due to its merging with F_2 when its height lowered in the afternoon (*see* Fig. 2).

The frequency of occurrence of $F_{1\cdot5}$ is a maximum an hour or so before noon in summer, at about noon in the equinoxes, and one hour after noon

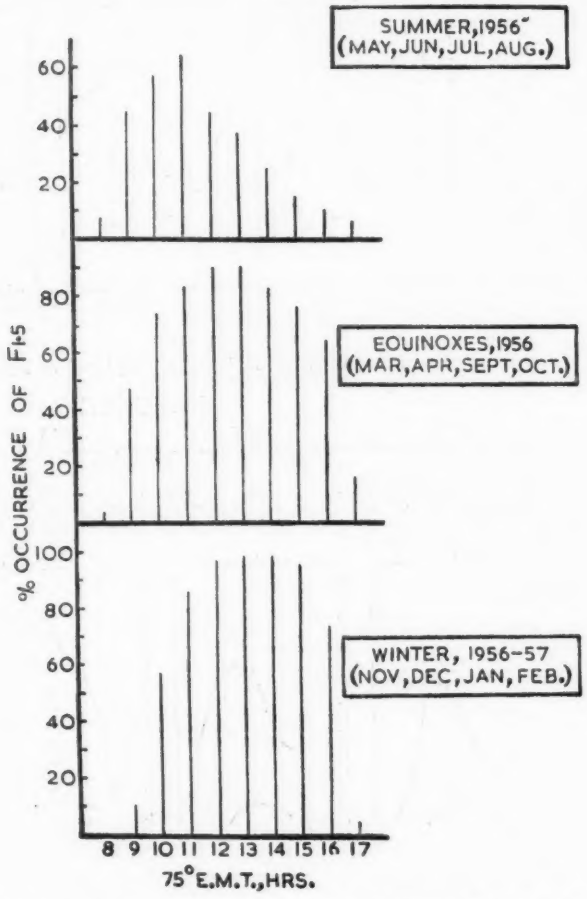
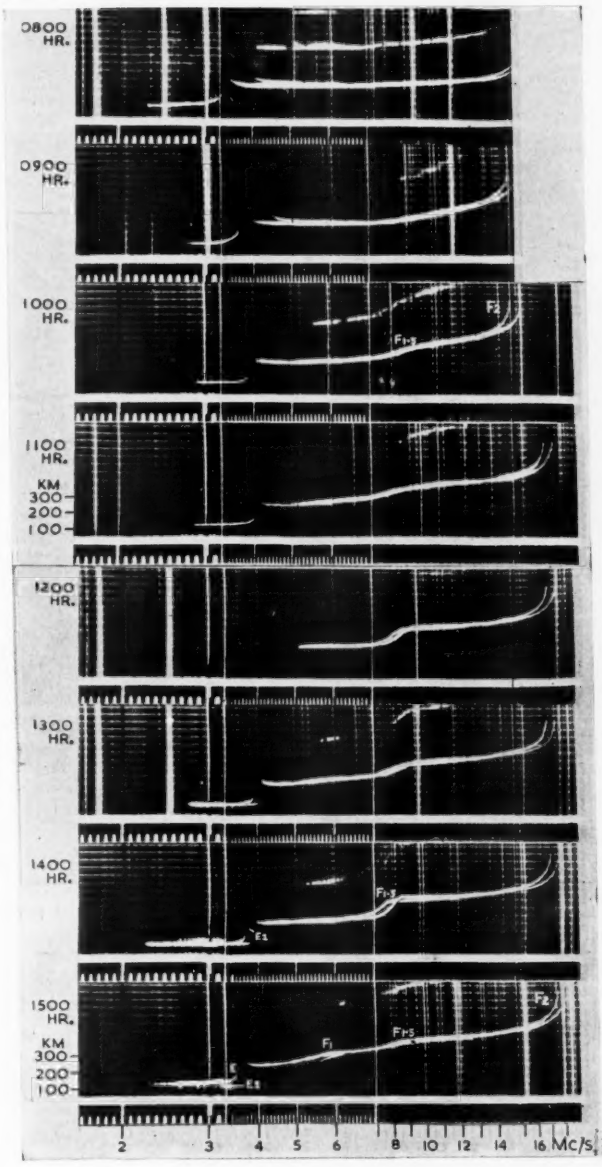
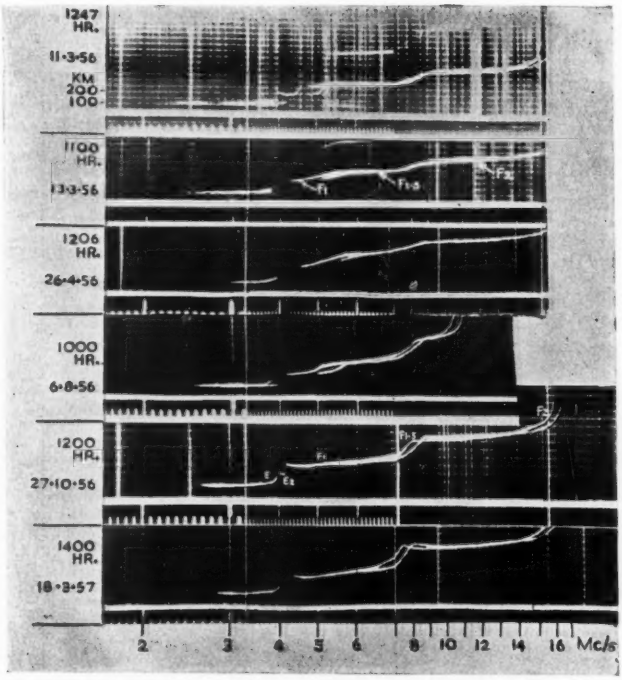


FIG. 4. Percentage occurrences of $F_{1\cdot5}$ at different hours of the day during the three seasons.



Hourly *h'-f* ionospheric records showing the $F_{1\cdot5}$ layer during daytime, Ahmedabad, November 13, 1956. (Faint portions in the records have been touched up for reproduction.).



Some examples of F_1, $F_{1\cdot5}$ and F_2 clearly recorded at Ahmedabad. (Faint portions in the records have been touched up for reproduction.)

in winter. These are approximately the times where *hp* F_2 is a maximum. Fig. 4 shows the percentage occurrences of $F_{1\cdot5}$ at different hours of the day during the three seasons of 1956–57.

The fact that *h'* $F_{1\cdot5}$ remains practically constant at the same height (about 250 km.) although *fo* $F_{1\cdot5}$ and *hp* F_2 change greatly, shows that its appearance is connected with some physical stratification of composition associated with a rapid change in the rate of recombination of electrons with height.

The layer forms when electrons are pushed up mechanically, by electromagnetic drift-forces. Its presence becomes more evident when the F_2 layer is already deep as over equatorial latitudes in summer, in high sunspot years or when magnetic and ionospheric disturbances cause temporary upheaval and expansion of the ionosphere. It is apparently formed by dynamical causes; after formation, the electron density slowly decays with time.

The study was undertaken at the suggestion, and under the guidance of Dr. K. R. Ramanathan.

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A MODIFIED GATING LOGIC TO IMPROVE THE SPEED OF OPERATION OF DOUBLE RANK COUNTERS

By B. K. Basu and P. V. S. Rao

(*Tata Institute of Fundamental Research, Bombay-1*)

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(Communicated by Professor B. Peters, F.A.SC.)

Abstract

The speed of operation of double rank counters can be increased by a suitable modification of the gating logic now being used. The improvement in speed, predicted on theoretical grounds, has been experimentally verified. The prescribed logic enables the use of both the ranks of the counter to advantage, one rank counting in the normal, and the other in the reverse fashion.

Introduction

The use of counters, in digital computers, for iterating a sequence of micro-operations a specified number of times is well established. A design requirement for such a counter may be prescribed as follows: Let t be the total time taken by the counting pulse to set up all the digit stages of the counter. Then t must be less than the time taken for one complete iteration of the sequence. Clearly, the faster the computer and smaller the length of the sequence being iterated, the smaller is the permissible value of t. In this paper a gating logic is described to reduce t much below the value required by double rank counters now being used.

In the counters normally being used, a situation may arise during the process of counting when the counting pulse can give rise to a carry chain from the lower to the higher order digit stages. This cumulative action of the carry will cause a delay in the setting up of the higher order digit stages of the counter. One way of reducing this time delay (*i.e.*, setting up time t) is to let the carry propagation be determined by the set up of the digit stages prior to the arrival of the counting pulse. The carry can thus be channelled through external circuits. With a single rank counter,[1] however, such an arrangement, requiring accurate timing of pulses, complicates the design. It was, therefore, considered worthwhile to investigate the possibility of working out a similar system with double rank counters.

The double rank counter.—The design philosophy of double rank counters originated with the computer group of the Institute of Advanced Studies[2]

(I.A.S.) at Princeton. Since then this type of counter has been used in almost all the computers of the I.A.S. type. An attractive feature of such a system is that one can ensure reliability by completely avoiding transient storage and gating elements.

In double rank counters two flip-flops are necessary for each digit stage. Counting is done by the mutual exchange of information between the corresponding flip-flops of the two ranks and requires a cycle of two pulses for each count. One rank, the false rank,* serves as a buffer or temporary storage space while the actual count is obtained in the true rank. Rules are formulated stating the conditions for gating from either rank to the other. A detailed analysis of the prevalent systems of gating arrangement has been published by Ware[3] and by Brown.[4] The cumulative carry delay is, however, not avoided in any of the systems described by them.

A gating logic for avoiding carry delay.—Consider a single stage counter containing a true (T) and a false (F) flip-flop. Counting is done by gating the number from the true to the false (down pulse) and the false to the true (up pulse). Since the true flip-flop has to change for every up pulse it is evident that one of the two, $T \rightarrow F$ or $F \rightarrow T$ transfers should be in the complement form† while the other is direct. For definiteness, let us assume that the gating from the true to the false flip-flop is direct and from the false to the true is in complement form. This can be symbolically represented as,

$$T \overset{d}{\rightarrow} F$$

$$F \overset{c}{\rightarrow} T$$

For a multi-stage counter the conditions for gating $T_i \rightarrow F_i$ and $F_i \rightarrow T_i$ can be readily derived in the following way. If one has to avoid the carry delay completely when the gating from the false to the true takes place, it is evident that this gating has to be done in parallel. We can, therefore, write down the condition of gating from the false to the true rank as,

$$F_i \overset{c}{\rightarrow} T_i, \text{ for } i = 0, 1, \ldots, n \text{ with every up pulse.} \qquad (1)$$

The above condition simply implies that the counting has actually been accomplished by the down pulse preceding the up pulse. Now the T_i of a particular stage i will change its state during any count if in the previous

* The terminology, true rank and false rank is taken from Ware. See reference 3.

† In this paper complement always means 1's complement.

setting of the true rank, the flip-flops from T_{i-1} down to T_0 have all been 1's. But T_i can change if and only if F_i changes. The rule for $T_i \to F_i$ can now be readily formulated as follows:

$$T_i \xrightarrow{d} F_i \text{ by the down pulse if all the stages } T_{i-1} \text{ to } T_0 \text{ are 1's.} \quad (2)$$

Combining (1) and (2), we have the complete gating rules as,

$$\text{(i) up pulse } F_i \xrightarrow{c} T_i, \text{ for } i = 0, 1, \ldots\ldots, n$$

$$\text{(ii) down pulse } T_i \xrightarrow{d} F_i, \text{ for } i = 1, \ldots, n, \text{ if the digit stages } T_{i-1} \text{ to } T_0 \text{ are all 1's} \quad (3)$$

$$\text{down pulse } T_0 \xrightarrow{d} F_0.$$

A logical diagram satisfying these gating rules is shown in Fig. 1.

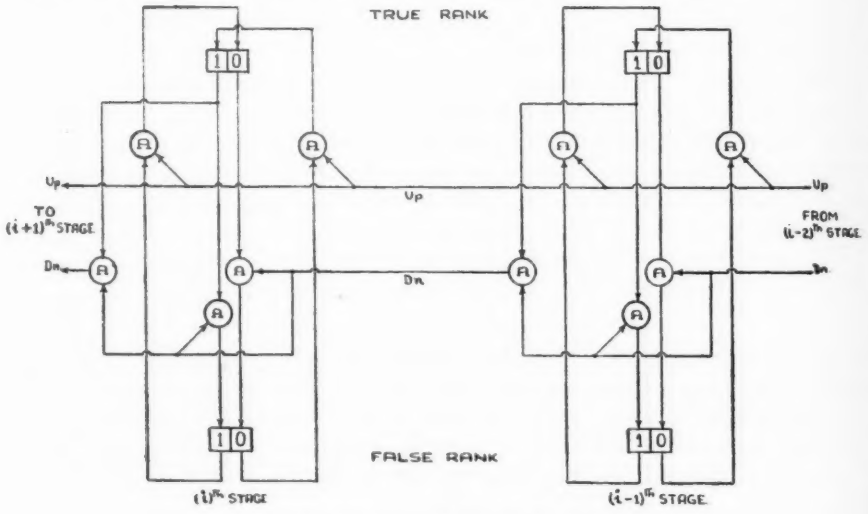

FIG. 1. Logical Diagram of Double Rank Counter.

Some distinct advantages of this system of gating can be easily seen. First of all, no carry delay is involved in gating from the false to the true rank by the up pulse which may be termed the counting pulse. Even in the gating from the true to the false rank, there is very little carry delay involved, since the carry is channelled through external circuits. If cathode follower type of negative ' And ' gates are used, the carry delay time will be negligible

for a six-stage shift counter of a typical digital computer. Secondly, since the false rank always contains the complement of the number in the true rank, the false rank counts down from the final number while the true rank counts up to it. Thus a single counter can serve the purpose of additive and subtractive counting at the same time.

In Table I, columns 2 and 3 give the readings of the true rank and the false rank of a four-stage counter just after the down shift has taken place. Column 4 also shows the number in the false rank when the gating arrangement is reversed, *i.e.*,

(i) up pulse $F_i \xrightarrow{d} T_i$, for $i = 0, 1, \ldots, n$

(ii) down pulse $T_i \xrightarrow{c} F_i$, for $i = 1, \ldots, n$ when T_{i-1} to T_0 are all 1's.

down pulse $T_0 \xrightarrow{c} F_0$. (4)

TABLE I

Countings of the true and the false ranks of a four stage counter

Decimal equivalent of the number in the true rank	Number in the true rank	Number in the false rank	
		$F \xrightarrow{c} T, T \xrightarrow{d} F$	$F \xrightarrow{d} T, T \xrightarrow{c} F$
0	0000	1110	0001
1	0001	1101	0010
2	0010	1100	0011
3	0011	1011	0100
4	0100	1010	0101
5	0101	1001	0110
6	0110	1000	0111
7	0111	0111	1000
8	1000	0110	1001
9	1001	0101	1010
10	1010	0100	1011
11	1011	0011	1100
12	1100	0010	1101
13	1101	0001	1110
14	1110	0000	1111
15	1111	1111	0000

This table makes it quite clear that counting actually takes place in the down shift from the true to the false rank. If the count in the false rank is

of no consequence, one can decide arbitrarily for each digit stage, which of the two transfers $F \rightarrow T$ or $T \rightarrow F$ is to be in complement form. In this case, however, it is to be expected that the numbers in the false rank will not follow the usual sequence.

EXPERIMENTAL RESULTS

To verify experimentally the advantage of the gating logic described, a four-stage counter was built and its performance was compared with that of a prevalent type of such counter. The initial condition was set up so that a single counting pulse gave rise to a carry chain from the lowest to the highest order stage of the counter. The setting up time was then measured with respect to the counting pulse. In the logic described in this paper, there can be a setting up delay only in the down shift, as in the up shift information from all the digit stages is gated in parallel. Therefore, measurement was made only when the number was being gated from the true to the false rank of the counter. It was found that the total setting up time in the new design was virtually the same as the setting up time of a single flip-flop, whereas, with the old design the time delay was nearly equal to four times this.

Counting from a predetermined number.—In some applications it is necessary for a counter to have arrangements so that counting may start from a predetermined number. For either of the gating arrangement 3 or 4 this can be accomplished by simply gating the predetermined number *plus* one in the false rank of the counter in complement (gating arrangement 3) or in true form (gating arrangement 4) and start the counting cycle with the up pulse. This is, of course, the same thing as gating the number without adding one in the false rank and applying one cycle of up and down pulse externally. However, if the carry delay consideration is not too stringent, the adding of one or the external cycling can be avoided by interchanging the role of the true and the false rank flip-flops, described before, in the following manner:

$$\begin{aligned}
&\text{(i) down pulse } T_i \xrightarrow{c} F_i \text{ for } i = 0, \ldots, n, \text{ in parallel.} \\
&\text{(ii) up pulse } F_i \xrightarrow{d} T_i \text{ for } i = 1, \ldots, n, \text{ if all the stages } F_{i-1} \text{ to F} \\
&\qquad \text{are zeros.} \\
&\text{up pulse } F_0 \xrightarrow{d} T_0. \qquad (5)
\end{aligned}$$

In this case counting is accomplished by the up shift instead of the down shift as in the other cases. For counting from a predetermined value

the required number is to be gated in the true rank of the counter and the counting cycle can be started with the down pulse first.

Conclusion

The gating logic for double rank counters was developed in an attempt to design a shift counter suitable for operation with a fast digital computer. Several other possible uses of such a counter have also been indicated in the paper. It has been found that the proposed change in the gating logic does not increase the complexity of the design of double rank counters any more than what is needed with the prevalent gating arrangement.

Acknowledgments

Thanks are due to Dr. D. Y. Phadke for his interest in the work. The authors are also grateful to Dr. R. Narasimhan for his helpful suggestions and encouragement.

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4. Brown, R. M. .. "Some notes on logical binary counters," *Trans. I.R.E.*, June 1955, **EC-4** (2), 67–69.

STUDIES WITH SCINTILLATION COINCIDENCE SPECTROMETER: Se^{75} and Sb^{125}

By Girish Chandra

(Tata Institute of Fundamental Research, Bombay-1)

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(Communicated by Professor B. Peters, F.A.Sc.)

Abstract

Cascade relationships between gamma-transitions in the decay of Se^{75} and Sb^{125} have been investigated with the help of a scintillation coincidence spectrometer. A decay scheme for Se^{75} has been proposed.

Selenium-75

The decay scheme of Se^{75} has been studied by a number of workers. It is well established that it decays by pure electron-capture process to As^{75}, which emits a large number of gamma-radiations. Jensen *et al.*[1] in their study of internal conversion and photo-electron spectra of this isotope find the following gamma-radiations: 66, 76, 98, 124, 138, 203, 268, 281, 307 and 405 Kev. Later Lu *et al.*[2] who studied this isotope by the summing technique using a scintillation spectrometer, concluded that—

(*a*) 405 Kev is the highest excited level.

(*b*) 138 Kev and 269 Kev radiations are in cascade.

(*c*) 124 Kev transition is in cascade with some gamma-transition whose energy is not known.

(*d*) 98 Kev transition is perhaps not in coincidence with any transition.

It was considered desirable to study this isotope in detail with the help of a 'Slow-Fast' scintillation coincidence spectrometer. This instrument has been described in an earlier paper.[3]

Results and Discussions

Gamma-spectra in coincidence with 138 Kev and 269 Kev transitions respectively were recorded and the following results were obtained:—

1. 138 Kev and 269 Kev transitions are found to be in coincidence in agreement with Jensen *et al.*[1] and Lu *et al.*[2] (Figs. 2 and 3).

2. 138 Kev transition is found to be in coincidence with 200 ± 5 Kev transition (Fig. 2 *b*) confirming the assumption of Jensen *et al.*[1] and Lu *et al.*[2]

3. A definite indication of a weak gamma-transition of about 95 ± 3 Kev, in cascade with 138 Kev (Fig. 2 *a*), has been found. Lu *et al.*[2] have

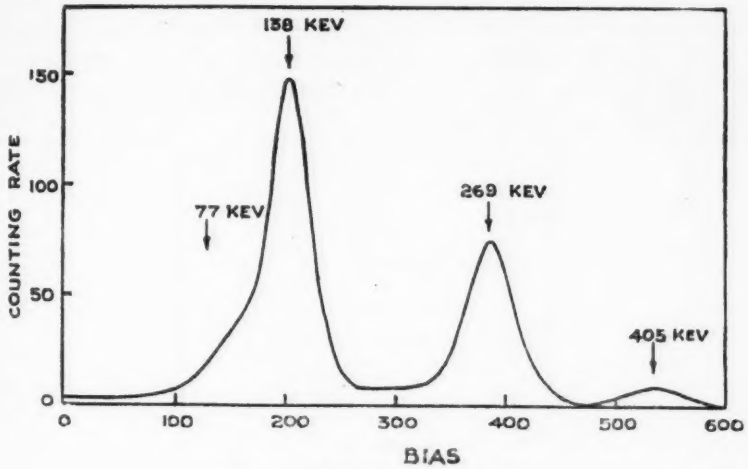

FIG. 1. Gamma Spectrum of Se^{75}.

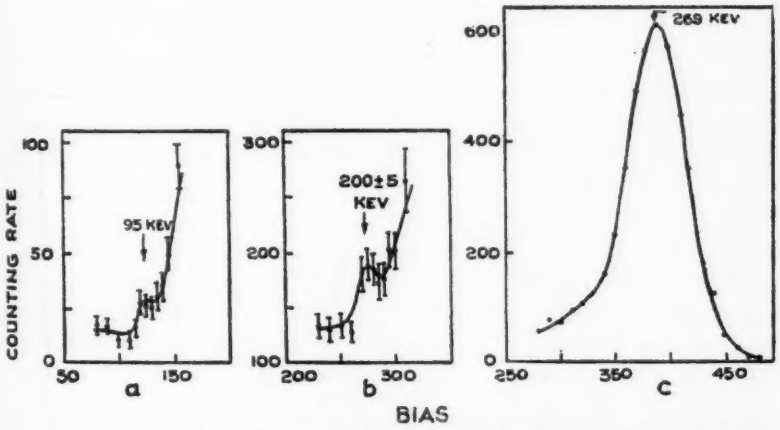

FIG. 2. Gamma Spectra in Coincidence with 138 KeV Gamma Radiations of Se^{75}.

found by summing technique that the 98 Kev transition is not in coincidence with any transition. Thus, there are possibly two transitions of nearly the same energy of 98 Kev.

4. Contrary to the assumption of Jensen *et al.*[1] and Lu *et al.*[2], 66 ± 3 Kev transition has been found to be in coincidence with 269 Kev transi-

tion and not with 138 Kev (Fig. 3). 77 Kev transition is not found to be in coincidence with either of 138 Kev or 269 Kev transitions.

5. Jensen *et al.*[1] and Lu *et al.*[2] infer 124 Kev and 280 Kev transitions to be in cascade. It has been shown by Lu *et al.*[2] that 124 Kev transition is in coincidence with some gamma-transition whose energy is not known. To check the assumption that 124 Kev and 280 Kev are in cascade the following experiment was performed:

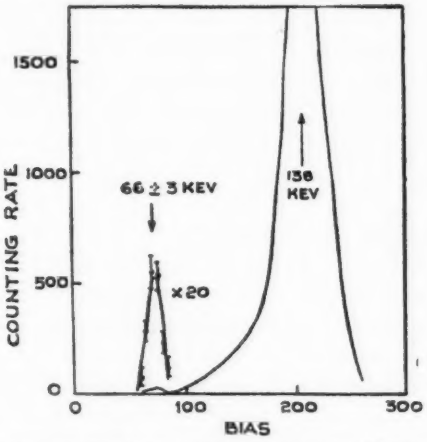

FIG. 3. Gamma Spectrum in Coincidence with 270 KeV of Se^{75}.

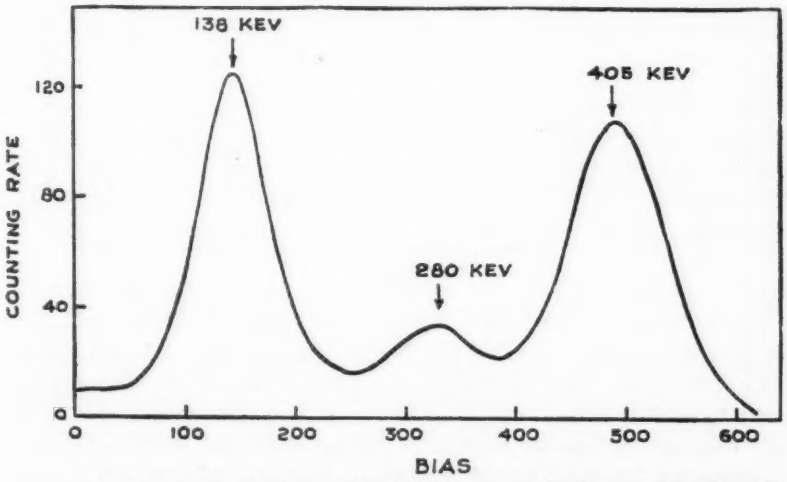

FIG. 4. Gamma Spectrum of Se^{75} with source at the Centre of the Crystal.

Gamma-spectrum of Se^{75} with the source at the centre of a $2'' \times 2''$ NaI (Tl) crystal was taken (Fig. 4). Since 138 Kev and 269 Kev peaks are summed up to 405 Kev, the peak at 280 Kev is easily brought out as a result of considerable reduction in the intensity of the 269 Kev peak which ordinarily would mask the 280 Kev line. Gamma-spectrum in coincidence with this 280 Kev is taken in the region of 124 Kev (Fig. 5). In this case the crystal of the other channel was kept opposite to the hole of the well-type crystal. In Fig. 5, the singles and coincidence spectra are shown normalised

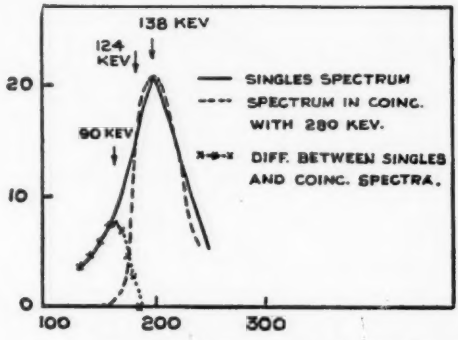

FIG. 5. Spectrum in Coincidence with 280 KeV of Se^{75}

at the peak. The difference between the two spectra gives a peak at about 90 Kev, showing that the coincidence spectrum does not contain 90 Kev line as expected but contains 138 Kev as well as 124 Kev lines. This indicates the possibility that the 124 Kev and 280 Kev transitions are in cascade.

On the basis of these results a modified decay scheme of Se^{75} is proposed (Fig. 6). This explains all the above mentioned results. Since the 77 Kev transition is not found to be in coincidence with either of 138 Kev and 269 Kev transitions, it is assumed that the 77 Kev level is mainly formed by the electron-capture process, 66 Kev transition being much weaker than the 77 Kev transition.

ANTIMONY-125

This isotope has been studied by a number of workers with the help of beta-ray spectrometers. It is found to have a complex beta spectrum[4] of energy groups at 621 Kev and 288 Kev. There were indications of lower energy groups but their energies could not be measured because of a large number of internal conversion lines. On the basis of beta-gamma coincidence experiments with a magnetic lens spectrometer Moreau[5] reported the following beta groups with maximum energy at 612, 444, 300 and 125 Kev.

Spectrometer studies[4] have shown the existence of the following gamma-transitions: 110, 125, 174, 431, 466, 609 and 646 Kev. It has been shown[6-8] that there exists an excited state of 145 Kev in Te^{125} which is a metastable state of a half-life of 58 days.

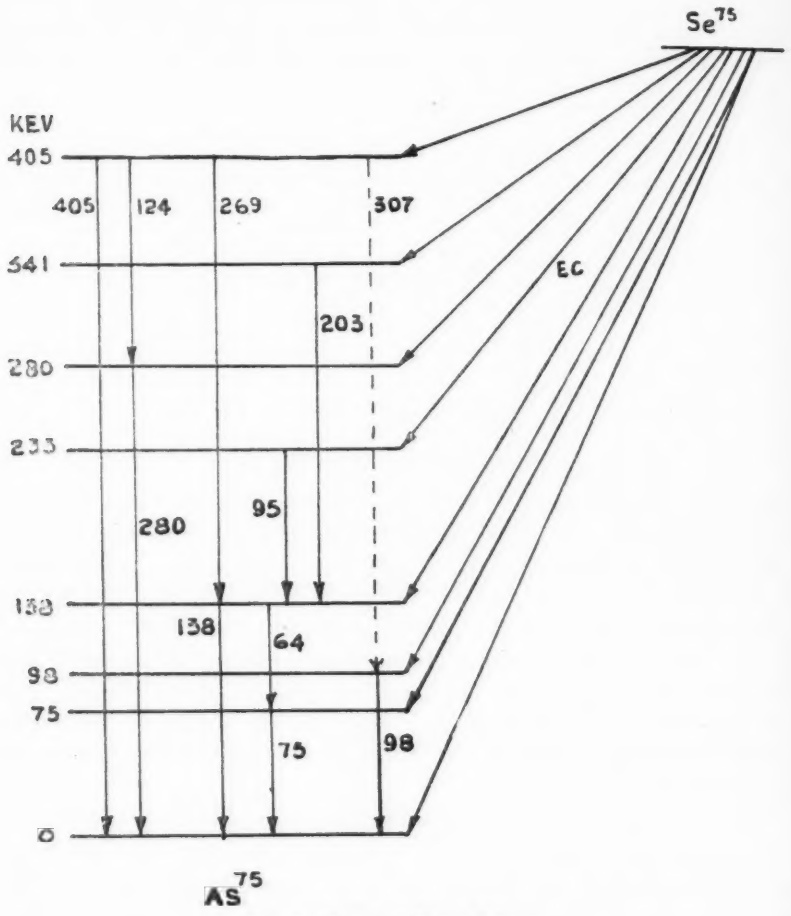

FIG. 6. Proposed Decay Scheme.

To establish the cascade relationships between different gamma-transitions in the decay of Sb^{125} coincidence studies were undertaken.

Results

Gamma-spectra in coincidence (Fig. 7) with 175 Kev and 427 Kev transitions respectively were taken with the following results:

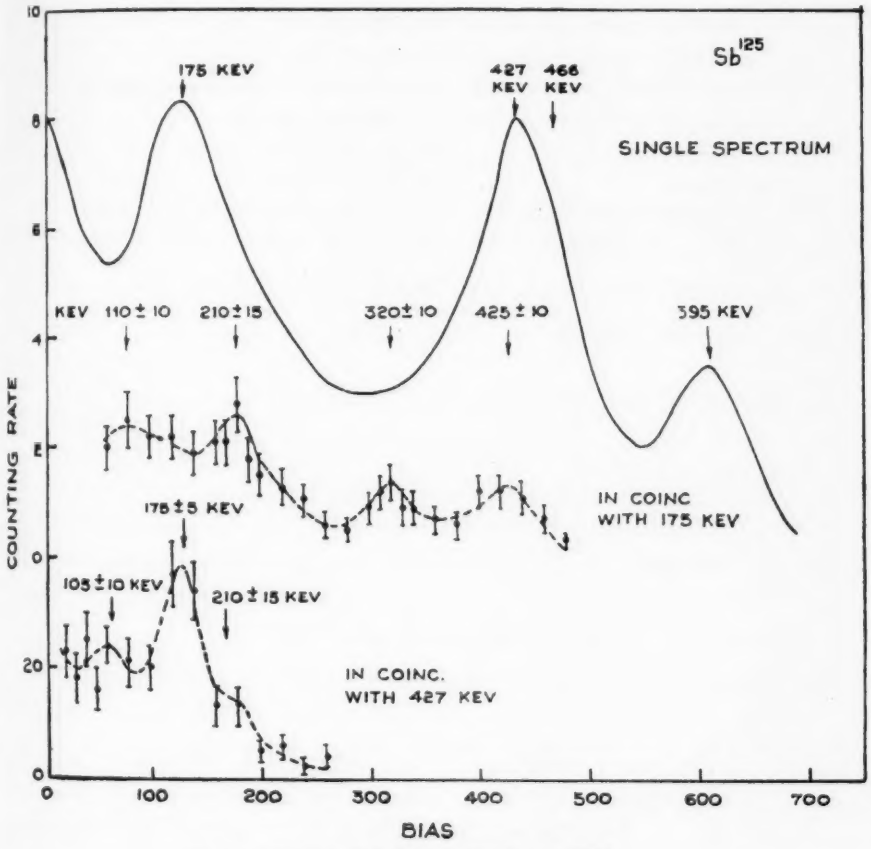

FIG. 7. Gamma Coincidence Spectra of Sb^{125}.

1. Gamma-transitions in coincidence with 175 Kev are found to be: 110 ± 10, 210 ± 15, 320 ± 10 and 425 ± 10 Kev.

2. Gamma-transitions in coincidence with 427 Kev are found to be: 105 ± 10, 175 ± 5 and 210 ± 15 Kev.

These results are in good agreement with those of a recent coincidence study by Lazar.[9]

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CHARACTERISTIC ROOTS OF THE PRODUCT OF CERTAIN MATRICES

By N. A. Khan

(*Muslim University, Aligarh*)

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1. Introduction

In a recent paper,[3] Bela Sz.-Nagy has proved the following result regarding the characteristic values $c(AB)$ of the product matric AB:—

$$c_{\min.}(AA^*)\, c_{\min.}(BB^*) \leq |c(AB)|^2 \leq c_{\max.}(AA^*)\, c_{\max.}(BB^*) \qquad (1)$$

where $c_{\min.}$ and $c_{\max.}$ stand respectively for the smallest and largest characteristic values.

In this paper we find limits for the characteristic roots of AB (i) in terms of the characteristic roots of A and B when both of these matrices are Hermitian (skew-Hermitian), and (ii) in terms of the characteristic roots of A, $(B + B^*)/2$ and $(B - B^*)/2i$ when A is Hermitian (skew-Hermitian) and B is any matrix. These results have been derived from (1).

In the sequel, Re $c(A)$ and Im $c(A)$ will denote, respectively, the real and imaginary parts of $c(A)$.

2. Upper Bound for $c(AB)$

Theorem 1. *Let A and B be two Hermitian matrices and let* $c(AB)$ *stand for any characteristic root of AB. Then*

$$|c(AB)| \leq [\max. |c(A)|]\,[\max. |c(B)|] \qquad (2)$$

We omit the proof of this theorem since it can be worked out easily with the help of Nagy's result and consider the following:—

Theorem 2. *Let A and B be two commuting matrices, such that one of them, say A, is Hermitian. If* $c(AB)$ *denotes an arbitrary characteristic root of AB then,*

$$\text{Re}\, c(AB) \leq [\max. |c(A)|]\left[\max. \left| c\left(\frac{B + B^*}{2}\right)\right|\right] \qquad (3)$$

and

$$\text{Im}\, c(AB) \leq [\max. |c(A)|]\left[\max. \left| c\left(\frac{B - B^*}{2i}\right)\right|\right] \qquad (4)$$

Proof.—Applying (1) to the product matrix AH, where $H = (B + B^*)/2$, we have

$$|c(AH)|^2 \leq c_{max.}(AA^*)\, c_{max.}(HH^*) = c_{max.}(A^2)\, c_{max.}(H^2)$$

This gives

$$c(AH) \leq [\text{max. } |c(A)|]\,[\text{max. } |c(H)|]. \tag{5}$$

We drop the sign of modulus from the left-hand side, since the characteristic roots of the Hermitian matrix AH are all real.

But, by a well-known result of Hirsch[2], we have

$$\begin{aligned} Re\, c(AB) &\leq c_{max.}\left(\frac{AB + (AB)^*}{2}\right) \\ &= c_{max.}\left(\frac{AB + B^*A^*}{2}\right) \\ &= c_{max.}\left(\frac{AB + A^*B^*}{2}\right), \text{ since } AB = BA \text{ implies} \\ &\qquad\qquad B^*A^* = A^*B^* \\ &= c_{max.}\left(\frac{AB + AB^*}{2}\right), \text{ since A is Hermitian} \\ &= c_{max.}(AH). \end{aligned}$$

Combining (5) with the above inequality, we have

$$Re\, c(AB) \leq [\text{max. } |c(A)|]\,[\text{max. } |c(H)|],$$

and inequality (3) is established.

To prove (4), we similarly apply (1) to the matrix AK, where $K = (B - B^*)/2i$, and have

$$c(AK) \leq [\text{max. } |c(A)|]\,[\text{max. } |c(K)|]. \tag{6}$$

Again, by a well-known result of Bromwich[1] we have

$$\begin{aligned} Im\, c(AB) &\leq c_{max.}\left(\frac{AB - (AB)^*}{2i}\right) \\ &= c_{max.}\left(\frac{AB - B^*A^*}{2i}\right) \\ &= c_{max.}\left(\frac{AB - AB^*}{2i}\right), \text{ since A is Hermitian and } AB = BA \\ &= c_{max.}(AK) \end{aligned}$$

Combining (6) with the above inequality, we obtain (4), which completes the proof of Theorem 2.

Let us now suppose that A is skew-Hermitian, so that iA is Hermitian and the inequality (3) takes the following form:

$$\mathrm{Im}\, c(AB) \leq [\max. |c(iA)|] \left[\max. \left| c\left(\frac{B + B^*}{2}\right)\right|\right],$$

since the real part of a characteristic root of A is equal to the imaginary part of the corresponding characteristic root of iA. Also, when A is skew-Hermitian, (4) changes to:—

$$\mathrm{Re}\, c(AB) \leq [\max. |c(iA)|] \left[\max. \left| c\left(\frac{B - B^*}{2i}\right)\right|\right].$$

Thus we have the following:—

Corollary.—Let A and B be two commuting matrices and let A be skew-Hermitian. Then for any characteristic root $c(AB)$ of AB

$$\mathrm{Re}\, c(AB) \leq [\max. |c(iA)|] \left[\max. \left| c\left(\frac{B - B^*}{2i}\right)\right|\right] \tag{7}$$

and

$$\mathrm{Im}\, c(AB) \leq [\max. |c(iA)|] \left[\max. \left| c\left(\frac{B + B^*}{2}\right)\right|\right]. \tag{8}$$

3. Remarks on the Lower Bounds of $c(AB)$

From (1) we can derive the following inequality:

$$[\min. |c(A)|] [\min. |c(B)|] \leq |c(AB)|, \tag{9}$$

when A and B are Hermitian.

In order to find limit for $\mathrm{Re}\, c(AB)$, when A is Hermitian and $AB = BA$ we can prove that

$$[\min. |c(A)|] [\min. |c(H)|] \leq |c(AH)|,$$

and

$$c_{\min.}(AH) \leq \mathrm{Re}\, c(AB), \text{ where } H = \frac{(B + B^*)}{2}.$$

Thus, if the Hermitian matrix A commutes with B and further the characteristic roots of $A(B + B^*)/2$ are all positive, we have the following inequality:—

$$[\text{min. } |c(A)|]\left[\text{min. } \left| c\left(\frac{B + B^*}{2}\right)\right|\right] \leq \text{Re } c(AB) \tag{10}$$

Similarly, we can establish the following:

$$[\text{min. } |c(A)|]\left[\text{min. } \left| c\left(\frac{B - B^*}{2i}\right)\right|\right] \leq \text{Im } c(AB), \tag{11}$$

if the Hermitian matrix A commutes with B and the characteristic roots of the Hermitian matrix $A(B - B^*)/2i$ are all positive.

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ON A FUNCTION OF RAMANUJAN

By Omar Ali Siddiqi

[*Senior Lecturer, Department of Mathematics, Muslim University, Aligarh (India)*]

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Section 1

Let

$$\phi(t) = \sum_{n=1}^{\infty} \frac{n^{n-2}}{\lfloor n-1} t^{n-1} e^{-nt} \text{ for } t \geqslant 1$$

denote Ramanujan function.[1] It was conjectured by Ramanujan that

$$(-1)^n \frac{d^n \phi}{dt^n} \geqslant 0 \text{ for } t \geqslant 1, \ n = 1, 2, 3, \ldots\ldots\ldots$$

The conjecture was proved by Auluck and Chowla[3] for $n = 1, 2, 3,$ and by Shah and Sharma[4] for $n = 1, 2, 3, 4$. In this note I prove the result

$$(-1)^n \left[\frac{d^n \phi(t)}{dt^n}\right]_{t=1+0} > 0 \text{ for } n = 1, 2, 3, \ldots\ldots\ldots$$

I indicate a method which gives an easy proof for small values of n. If n is larger than the method in para 5 proves the conjecture for $t > n$ but the proof for $t < n$ for large values of n becomes complicated.

Section 2

Theorem I.

$$(1-\omega)\,\omega_n + (\omega_{n-1} - \phi_{n-1}) = \sum_{r=1}^{\frac{n-1}{2}} {}^nC_r \omega_r \omega_{n-r}$$

or

$$= \sum_{r=1}^{\frac{n-2}{2}} {}^nC_r \omega_r \omega_{n-r} + \tfrac{1}{2}{}^nC_r \omega_{n/2}{}^2$$

according as n is odd or even.

Proof.—$\phi(t)$ and its derivatives are continuous functions for $t > 1$. From

$$\omega e^{-\omega} = te^{-t}$$

$$(1-\omega)\,\omega_1 = (1-t)\,\phi$$

next

$$(1-\omega)\,\omega_2+(\omega_1-\phi_1)=\omega_1{}^2=\tfrac{1}{2}\,{}^2C_1\omega_1{}^2$$

similarly

$$(1-\omega)\,\omega_3+(\omega_2-\phi_2)=3\,\omega_1\omega_2={}^3C_1\omega_1\omega_2$$

$$(1-\omega)\,\omega_4+(\omega_3-\phi_3)=4\,\omega_1\omega_3+3\,\omega_2{}^2={}^4C_1\omega_1\omega_3+\\+\tfrac{1}{2}\,{}^4C_2\omega_2{}^2$$

$$(1-\omega)\,\omega_5+(\omega_4-\phi_4)={}^5C_1\,\omega_1\omega_4+{}^5C_2\omega_2\omega_3$$

$$(1-\omega)\,\omega_6+(\omega_5-\phi_5)={}^6C_1\omega_1\omega_5+{}^6C_2\omega_2\omega_4+\tfrac{1}{2}\,{}^6C_3\omega_3{}^2$$

Suppose the relation is true for the nth value, *i.e.*,

$$(1-\omega)\,\omega_n+(\omega_{n-1}-\phi_{n-1})$$

$$=\sum_{r=1}^{\frac{n-1}{2}}{}^nC_r\omega_r\omega_{n-r}\quad\text{for } n \text{ odd}$$

$$=\sum_{r=1}^{\frac{n-2}{2}}{}^nC_r\omega_r\omega_{n-r}+\tfrac{1}{2}{}^nC_{n/2}\omega_{n/2}{}^2\quad\text{for } n \text{ even}$$

by actual differentiation.

$$(1-\omega)\,\omega_{n+1}+(\omega_n-\phi_n)$$

$$=({}^nC_0+{}^nC_1)\,\omega_1\omega_n+({}^nC_1+{}^nC_2)\,\omega_2\omega_{n-1}+\ldots.\\+\left({}^nC_{\frac{n-3}{2}}+{}^nC_{\frac{n-1}{2}}\right)\omega_{\frac{n-1}{2}}\,\omega_{\frac{n+3}{2}}+{}^nC_{\frac{n-1}{2}}\,\omega_{\frac{n+1}{2}}{}^2$$

or

$$(1-\omega)\,\omega_{n+1}+(\omega_n-\phi_n)$$

$$={}^{n+1}C_1\omega_1\omega_n+{}^{n+1}C_2\omega_2\omega_{n-1}+\ldots\ldots\ldots\\+{}^{n+1}C_{\frac{n-1}{2}}\,\omega_{\frac{n-1}{2}}\,\omega_{\frac{n+3}{2}}+\tfrac{1}{2}{}^{n+1}C_{\frac{n+1}{2}}\,\omega_{\frac{n+1}{2}}{}^2$$

or

$$(1-\omega)\,\omega_{n+1}+(\omega_n-\phi_n)$$

$$=\sum_{r=1}^{\frac{(n+1)-2}{2}}{}^{n+1}C_r\omega_r\omega_{(n+1)-r}+\tfrac{1}{2}{}^{n+1}C_{\frac{n+1}{2}}\,\omega_{\frac{n+1}{2}}{}^2$$

here $(n+1)$ is even and it satisfies condition (2) above. A similar procedure is followed for the even value of λ. The theorem is thus proved from the principle of induction.

THEOREM II.

$$\omega_n = n\phi_{n-1} + \phi_n t$$

This follows by direct successive differentiation of

$$\omega = \phi t$$

Section 3

Let the values of ϕ, ϕ_1, ϕ_2, etc., and ω, ω_1, ω_2, etc., at $t = 1 + 0$ and $\omega = 1 - 0$ be respectively denoted by $\bar{\phi}$, $\bar{\phi}_1$, $\bar{\phi}_2$, etc., and $\bar{\omega}$, $\bar{\omega}_1$, $\bar{\omega}_2$, etc.

Now

$$\bar{\phi} = 1$$

So

$$\bar{\omega} = 1$$

Further from Theorems I and II $\bar{\omega}_1 = \bar{\phi}, + \bar{\phi}_1 = 1 + \bar{\phi}_1$ and $\bar{\omega}_1 - \bar{\phi}_1 = \bar{\omega}_1^2$ giving $\bar{\phi}_1 = -2$ and $\bar{\omega}_1 = -1$.

Similarly,

$$\bar{\omega}_2 = 2\bar{\phi}_1 + \bar{\phi}_2 = -4 + \bar{\phi}_2 \text{ and } \bar{\omega}_2 - \bar{\phi} = 3\,\bar{\omega}_1\bar{\omega}_2$$

So

$$\bar{\omega}_2 = \frac{4}{3} \text{ and } \bar{\phi}_2 = \frac{16}{3}$$

Next

$$\bar{\omega}_3 = 3\bar{\phi}_2 + \phi_3 \text{ and } \bar{\omega}_3 - \bar{\phi}_3 = 4\bar{\omega}_1\bar{\omega}_3 + 3\bar{\omega}_2^2$$

So

$$\bar{\omega}_3 = -\frac{8}{3} \text{ and } \bar{\phi}_3 = -\frac{56}{3}$$

In this way

$$\phi_1(1 + 0) = -2$$

$$\phi_2(1 + 0) = \frac{16}{3}$$

$$\phi_3(1 + 0) = -\frac{56}{3}$$

$$\phi_4(1+0) = \frac{3712}{45}$$

$$\phi_5(1+0) = -\frac{11968}{27}.$$

Thus a general method for determining any number of members of the sequence $\phi_1(1+0)$, $\phi_2(1+0)$, $\phi_3(1+0)$, etc., is developed. The direct differentiation method used by Auluck and Chowla and others becomes unworkable after $n = 5$ as the differentiations are lengthy and huge and the connected inequalities are complicated.

Section 4

The sets of relations in Theorem I can be expressed in the form

$$(1-\omega)\, t\phi_2 + (1-2\omega)\,\phi_1 + \omega_1 = {\omega_1}^2$$

$$(1-\omega)\, t\phi_3 + (2-3\omega)\,\phi_2 + \omega_2 = 3\,\omega_1\omega_2$$

$$(1-\omega)\, t\phi_4 + (3-4\omega)\,\phi_3 + \omega_3 = 4\,\omega_1\omega_3 + 3{\omega_2}^2$$

$$(1-\omega)\, t\phi_5 + (4-5\,\omega)\phi_4 + \omega_4 = 5\omega_1\omega_4 + 10\omega_2\omega_3$$

. . . . . .

. . . . . .

$$(1-\omega)\, t\phi_n + \{(n-1) - n\omega\}\,\phi_{n-1} + \omega_{n-1}$$

$$= \sum_{r=1}^{\frac{n-1}{2}} {}^nC_r\omega_r\omega_{n-r}$$

$$= \sum_{r=1}^{\frac{n-2}{2}} {}^nC_r\omega_r\omega_{n-r} + \tfrac{1}{2}{}^nC_{n/2}{\omega_{n/2}}^2$$

as n is odd or even.

From Equation (1) Section (2)

$$\omega_1 < 0 \text{ for } t > 1.$$

Hence $\bar{\omega}_1 < 0$ and so from Theorem II, $\bar{\phi}_1 < 0$. Now from (ii) above

$\bar{\omega}_2 - \bar{\phi}_2 = 3\bar{\omega}_1\bar{\omega}_2$ using Theorem II, $2\bar{\phi}_1 = 3\bar{\omega}_1\bar{\omega}_2$

Hence

$$\bar{\omega}_2 = \frac{2\bar{\phi}_1}{3\bar{\omega}_1} > 0 \text{ and so } \bar{\phi}_2 > 0.$$

Next

$$\bar{\omega}_3 - \bar{\phi}_3 = 4\bar{\omega}_1\bar{\omega}_3 + 3\bar{\omega}_2 \text{ or } 3\bar{\phi}_2 - 4\bar{\omega}_1\bar{\omega}_3 > 0$$

$$\therefore \quad \bar{\omega}_3 < \frac{3\bar{\phi}_2}{4\bar{\omega}_1} < 0 \text{ and so } \bar{\phi}_3 < 0$$

Similarly,

$$4\bar{\phi}_3 - 5\bar{\omega}_1\omega_4 < 0 \text{ or } \bar{\omega}_4 > \frac{4\bar{\phi}_3}{5\bar{\omega}_1} > 0 \text{ and so } \bar{\phi}_4 > 0$$

Let n be odd, so that $n\bar{\phi}_{n-1} - (n+1)\,\bar{\omega}_1\bar{\omega}_n < 0$, *i.e.*, $\bar{\omega}_n < 0$ and so $\bar{\phi}_n < 0$.

Now for $(n+1)$th value we have $(n+1)\,\bar{\phi}_n - (n+2)\,\bar{\omega}_1\bar{\omega}_{n+1} < 0$

Hence

$$\bar{\omega}_{n+1} > 0 \text{ and so } \bar{\phi}_{n+1} > 0.$$

Similarly for even value of n. Hence from the principle of induction whether n is even or odd $(-1)^n\, d^n\phi/dt^n > 0$.

Thus the conjecture is proved for $t = 1 + 0$ or

$$(-1)^n \left[\frac{d^n\phi(t)}{dt^n}\right]_{t+0} > 0 \text{ for } n = 1, 2, 3, \ldots\ldots$$

Section 5

THEOREM III.

$$\phi_{n+1} = {}^nC_0\phi\omega_{n+1} + {}^nC_1\phi_1\omega_n + {}^nC_2\phi_2\omega_{n-1} + \ldots + {}^nC_n\phi_n\omega_1 - \phi_n.$$

Proof.—From $\omega e^{-\omega} = te^{-t}$ we have $\phi e^{-\omega} = e^{-t}$

hence

$$\phi_1 = \phi\omega_1 - \phi.$$

Differentiating successively,

$$\phi_{n+1} = {}^nC_0\phi\omega_{n+1} + {}^nC_1\phi_1\omega_n + {}^nC_2\phi_2\omega_{n-1} + \ldots. + {}^nC_n\phi_n\omega_1 - \phi_n.$$

Section 6

THEOREM IV.

If $t \geqslant n$ where n is an integer, $(-1)^r\, d^r\phi/dt^r > 0$ for $r = 1, 2, \ldots. n$.

From Theorem II,

$$\omega_n = t\phi_n + n\phi_{n-1}$$

now

$$\phi_1 = \phi\omega_1 - \phi \text{ or } t\,\phi_1 = \omega\omega_1 - \omega$$

or

$$\omega_1 - \phi = \omega\omega_1 - \omega \text{ or } (1-\omega)\,\omega_1 = \phi - \omega = \phi\,(1-t)$$

this gives $\omega_1 < 0$ hence from $\omega_1 = t\phi_1 + \phi$ we get $\phi_1 < 0$

next $\phi_2 = \phi\omega_2 + \phi_1\omega_1 - \phi_1$ or $\omega_2 - 2\phi_1 = \omega\omega_2 + t\phi_1\omega_1 + t\phi_1$ or $(1-\omega)\,\omega_2 = t\phi_1\omega_1 + (2-t)\,\phi_1$ if $t \geqslant 2$ then $\omega_2 > 0$ and hence from $\omega_2 = t\phi_2 + 2\phi_1$ we have $\phi_2 > 0$ or $(-1)^2\, d^2\phi/dt^2 > 0$. Similarly $(1-\omega)\,\omega_3 = 2t\phi_1\omega_2 + t\phi_2\omega_1 + (3-t)\,\phi_2$.

If $t \geqslant 3$ then $\omega_3 < 0$ hence from $\omega_3 = t\phi_3 + 3\phi_2$ we have

$$\phi_3 < 0, \textit{ i.e.}, (-1)^3\, d^3\phi/dt^3 > 0.$$

Suppose the result is correct for the nth value, *i.e.*,

$$(1-\omega)\,\omega_n = t^{n-1}C_1\phi_1\omega_{n-1} + t^{n-1}C_2\phi_2\omega_{n-2} + \ldots\ldots + (n-t)\,\phi_{n-1}$$

and for

$$t \geqslant n,\ (-1)^n\omega_n > 0 \text{ and } (-1)^n\, d^n\phi/dt^n > 0$$

now from this result and the usual steps

$$(1-\omega)\,\omega_{n+1} = t^nC_1\phi_1\omega_n + t^nC_2\phi_2\omega_{n-1} + \ldots\ldots + \{(n+1)-t\}\phi_n$$

and if $t > n+1$, $(-1)^{n+1}\,\omega_{n+1} > 0$ and so $(-1)^{n+1}\,\phi_{n+1} > 0$ thus the theorem follows from the principle of induction.

This proves the conjecture $(-1)^r\, d^r\phi/dt^r > 0$

for all integral values of r less than n provided, $t \geqslant n$.

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POLAROGRAPHIC BEHAVIOUR OF METALS IN ETHANOLAMINES

Part V. Copper*

By R. S. Subrahmanya

(*Department of General Chemistry, Indian Institute of Science, Bangalore-3*)

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Introduction

Jessop[1] has obtained a single polarographic wave in triethanolamine solutions containing sodium hydroxide but concludes that the measurement of diffusion current is difficult as there is a rounding off at the diffusion current plateau. In their investigations on the preparation of metallic complexes of ethanolamines, Hieber and Levy[2] have not been able to isolate any complex of copper with triethanolamine. Investigations conducted in this laboratory have shown that, as in the case of cadmium,[3] nickel[4] and cobalt,[5] all the three amines form complexes with copper and under certain conditions give reduction waves of analytical utility. In the present communication, the results of a detailed investigation of the polarographic behaviour of ethanolamine complexes of copper are presented.

Experimental

The procedure employed in the present work has been essentially the same as that described previously.[6] A.R. copper sulphate is employed for the preparation of standard solutions. The temperature of recording the polarograms has been $30° \pm 0{\cdot}1°$ C. The droptime t has been adjusted to 5 seconds in 1 N potassium chloride and the values of m of the capillaries used have been 1·370, 1·227 and 1·150 mg. per second.

Results

1. *Effect of pH.*—Polarograms of cupric copper at pH 7·20, 6·50 and 5·40 for solutions containing 0·1 M triethanolamine are given in Fig. 1. 0·005% gelatin has been incorporated in solutions of pH 7·2 and below to suppress the maximum. It is evident that there are two poorly separated waves (A_1, A_2, A_3) in all the cases. It has been observed that between pH 7·2 and 12 the polarograms consist essentially of a single wave. At high pH values (above 12), the curvature of the wave just before the diffusion current

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plateau gets elongated and pressed inside. The properties of the polarograms at various pH values are presented in Table I.

TABLE I

Effect of pH on the polarographic behaviour of copper in presence of ethanolamines

Concentration of the amine 0·1 molar

Amine used	pH	Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt)	$E_{\frac{1}{4}} - E_{\frac{1}{2}}$ (Volt)
Monoethanolamine	6·50*	−0·03	0·030
	9·45	−0·21	0·029
	11·00	−0·35	0·028
	12·70	−0·43	0·031
	13·50	−0·47	0·029
Diethanolamine	6·05*	−0·03	0·029
	9·45	−0·22	0·030
	10·70	−0·33	0·032
	12·70	−0·44	0·028
	13·50	−0·50	0·029
Triethanolamine	5·55*	−0·014 poorly	0·029
		−0·10 separated	0·036
	6·50*	−0·01 poorly	0·023
		−0·12 separated	0·040
	7·20*	−0·049 poorly	0·026
		−0·13 separated	0·032
	8·65	−0·18	0·034
	9·70	−0·22	0·056
	11·10	−0·33	0·025
	12·70	−0·45	0·036
	13·50	−0·53	0·038

* 0·005% gelatin has been included in the base solutions to eliminate the maxima which appear only in these solutions.

The results indicate that the half-wave potentials of the two poorly separated waves decrease with decrease in pH. Further, the value of $E_{\frac{1}{4}} - E_{\frac{1}{2}}$ is of the order of 0·030 V showing the reversibility of the reduction process. Figure 1 also indicates that the height of the first wave increases at the expense of the second, the total height remaining almost the same. Above pH 7·2 the half-wave potential of the single wave increases with pH, the value of $E_{\frac{1}{4}} - E_{\frac{1}{2}}$ being about 0·030 V. At high pH values (12·7 and above) the

apparent value of $E_{\frac{1}{4}}-E_{\frac{3}{4}}$ is of the order of 0·050 V, while by applying correction for the bend, the value is reduced to about 0·030 V. It has to be pointed out that the numerical values for reversibility and half-wave potential are only approximate on account of the ill-defined nature of the doublet and the elongated nature of the bend before the diffusion current plateau.

The polarograms obtained with mono- and diethanolamines as complexing agents also exhibit maxima below pH 7, which can be suppressed by gelatin. In contrast to the behaviour of the triethanolamine complex, these complexes exhibit essentially a single reversible polarographic wave throughout the entire pH range studied.

2. *Effect of variation of the composition of the base electrolyte.*—Sodium hydroxide, sodium carbonate and ammonium chloride-ammonium hydroxide have been employed in the base solution as pH altering reagents to study the nature of the complexes produced.

(*a*) *Sodium hydroxide.*—The polarograms given in Figs. 2, 3, 4 and 5 show the effect of concentration of sodium hydroxide at different concentrations of tri- and monoethanolamines. Curves obtained with diethanolamine are similar in nature to those obtained with monoethanolamine. It is evident from a study of these curves that with an increase in the concentration of sodium hydroxide, when triethanolamine is employed as the complexing agent, there is a tendency for the splitting of the wave into two (Fig. 2). When the concentration of sodium hydroxide is kept constant, increase in the concentration of triethanolamine merely alters the slope of the polarographic wave. The properties of the waves obtained under various conditions are given in Table II.

In the case of mono- (Fig. 5) and diethanolamines there is practically no tendency for the splitting of the wave. The results presented in Table II indicate that the waves obtained in mono- and diethanolamine media are reversible while those obtained in triethanolamine have varying degrees of reversibility.

(*b*) *Sodium carbonate.*—In solutions containing 0·02 M triethanolamine one wave is obtained. Further, there is a progressive decrease in the slope of the wave with an increase in the concentration of triethanolamine without having any effect on the bends of the polarographic waves.

The mono- and diethanolamine complexes on the other hand exhibit only reversible waves. At low concentrations (0·02 M) of ethanolamine, however, the wave is slightly irreversible. The analysis of the waves is

TABLE II

Effect of sodium hydroxide on the polarographic behaviour of copper in presence of ethanolamines

Amine used	Concentration of		Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt)	$E_{\frac{1}{4}} - E_{\frac{1}{2}}$ (Volt)
	Amine (molar)	Sodium hydroxide (molar)		
Monoethanolamine	0·02	0·10	−0·388	0·027
	0·10	0·10	−0·430	0·031
	0·50	0·10	−0·468	0·028
	1·00	0·10	−0·487	0·028
	0·02	1·00	−0·452	0·036
	0·10	1·00	−0·469	0·029
	0·30	1·00	−0·501	0·031
	0·50	1·00	−0·513	0·032
	0·60	1·00	−0·523	0·032
	1·00	1·00	−0·532	0·032
Diethanolamine	0·02	0·10	−0·414	0·038
	0·10	0·10	−0·438	0·028
	0·30	0·10	−0·465	0·020
	0·60	0·10	−0·480	0·026
	0·02	1·00	−0·474	0·026
	0·10	1·00	−0·495	0·029
	0·40	1·00	−0·515	0·031
	1·00	1·00	−0·537	0·029
Triethanolamine	0·02	0·10	−0·444 (Sharp bend)	0·030
	0·10	0·10	−0·452 (Fairly sharp bend)	0·036
	0·50	0·10	−0·543 (Fairly sharp bend)	0·126
	0·70	0·10	−0·567 (Fairly sharp bend)	0·147
	1·00	0·10	−0·573 (Fairly sharp bend)	0·146
	0·02	1·00	−0·519 −0·710 (Bend not sharp) $E_{\frac{1}{4}}$ − $E_{\frac{1}{2}}$ and $E_{\frac{1}{2}}$ are corrected for the bend	0·033
	0·30	1·00	−0·569 (Bend not sharp. The presence of second wave is evident)	0·086
	0·50	1·00	−0·599	0·108
	0·70	1·00	−0·614	0·115
	1·00	1·00	−0·633	0·114
	0·02	5·00	−0·571 −0·745	0·034

summarized in Table III. The results are similar to those obtained in the case of sodium hydroxide solution.

TABLE III

Effect of sodium carbonate on the polarographic behaviour of copper in ethanolamines

Amine used	Concentration of		Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt)	$E_{\frac{1}{2}} - E_{\frac{1}{4}}$ (Volt)
	Amine (molar)	Sodium carbonate (molar)		
Monoethanolamine	0·02	0·10	−0·289	0·032
	0·10	0·10	−0·363	0·027
			Small wavelet at − 0·3 V	
	0·30	0·10	−0·385	0·029
	0·60	0·10	−0·403	0·028
	1·00	0·10	−0·432	
			Two waves very near each other	
	0·02	1·00	−0·312	0·039
	0·10	1·00	−0·368	0·030
	0·30	1·00	−0·399	0·034
	0·60	1·00	−0·428	0·040
	1·00	1·00	−0·450	
			Two waves very near each other	
Diethanolamine	0·02	0·10	−0·285	0·030
			−0·331	0·020
	0·10	0·10	−0·312	0·045
			−0·351	0·020
	0·25	0·10	−0·385	0·028
	0·60	0·10	−0·397	0·036
	1·00	0·10	−0·420	0·037
	0·02	1·00	−0·311	0·039
	0·10	1·00	−0·358	0·031
	0·40	1·00	−0·400	0·031
	1·00	1·00	−0·426	0·033
Triethanolamine	0·02	0·10	−0·298	0·036
	0·10	0·10	−0·340	0·046
	0·50	0·10	−0·496	0·131
	1·00	0·10	−0·524	0·146
	0·02	1·00	−0·324	0·041
	0·10	1·00	−0·350	0·029
			Only one wave, sharp bend	
	0·50	1·00	−0·432	0·087
	1·00	1·00	−0·486	0·114
			Only one wave, sharp bend	

(*c*) *Ammonium chloride* (1 *M*)-*Ammonium hydroxide* (1 *M*).—The results of the analysis of the polarographic waves obtained with mono-, di- and triethanolamines in presence of ammonium chloride-ammonium hydroxide are given in Table IV. A doublet is obtained in all the cases. The results indicate that the half-wave potentials of the first and the second waves remain nearly constant. The values of $E_{\frac{1}{4}} - E_{\frac{1}{2}}$ of the first wave is of the order of 0·045 V while that for the second wave is of the order of 0·065 V. In triethanolamine solutions, it has been found that the height of the first reduction wave progressively diminishes. In the case of the second wave, the value has been found to slightly increase to begin with and then fall progressively.

3. *Effect of concentration of copper on the diffusion current constant in base solutions containing ethanolamines.*—In Table V are presented the results

TABLE IV

Effect of ammonium chloride (1 *M*)-*ammonium hydroxide* (1 *M*) *on the polarographic behaviour of copper in presence of ethanolamines*

Amine used	Concentration of the amine (molar)	First wave		Second wave		Ratio of the height of the second wave to first wave
		Half-wave potential $E_{\frac{1}{4}}$ *vs.* S.C.E. (Volt)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (Volt)	Half-wave potential $E_{\frac{1}{4}}$ *vs.* S.C.E. (Volt)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (Volt)	
Monoethanolamine	0·02	ca. −0·22	0·044	ca. −0·49	0·054	1·15
	0·10	−0·22	0·043	−0·48	0·061	1·16
	0·50	−0·23	0·052	−0·49	0·062	1·03
	1·00	−0·25	0·059	−0·51	0·070	1·02
Diethanolamine	0·02	−0·22	0·042	−0·49	0·062	1·15
	0·10	−0·23	0·043	−0·49	0·058	1·08
	0·50	−0·23	0·045	−0·49	0·053	1·06
	1·00	−0·23	0·054	−0·50	0·056	1·02
Triethanolamine	0·002	−0·23	0·050	−0·50	0·062	0·88
	0·020	−0·23	0·040	−0·50	0·064	1·12
	0·10	−0·23	0·050	−0·50	0·065	1·17
	0·30	−0·23	0·045	−0·50	0·070	1·16
	0·60	−0·23	0·045	−0·51	0·075	1·32
	1·00	−0·23	0·045	−0·51	0·068	1·45

TABLE V

*Effect of concentration of copper on the diffusion current constant**

Concentration of copper (Millimolar)	Diffusion current constant $\frac{i_d}{Cm^{2/3}\,t^{1/6}}$	Concentration of copper (Millimolar)	Diffusion current constant $\frac{i_d}{Cm^{2/3}\,t^{1/6}}$
1. B.S.: 0·10 M Moen + 0·10 M NaOH + 0·005% gelatin X = 1·462 at −0·7 V *vs.* S.C.E.		9. B.S.: 0·10 M Moen + 0·10 M Na_2CO_3 + 0·005% gelatin X = 1·464 at − 0·7 V *vs.* S.C.E.	
1·022	3·82	1·022	3·81
10·80	3·77	10·80	3·77
2. B.S.: 0·10 M Moen + 1·00 M NaOH + 0·005% gelatin X = 1·462 at −0·7 V *vs.* S.C.E.		10. B.S.: 0·10 M Moen + 1·00 M Na_2CO_3 + 0·005% gelatin X = 1·464 at − 0·7 V *vs.* S.C.E.	
1·022	3·63	1·022	3·12
10·80	3·58	10·80	3·12
3. B.S.: 0·10 M Dien + 0·10 M NaOH + 0·005% gelatin X = 1·462 at −0·7 V *vs.* S.C.E.		11. B.S.: 0·10 M Dien + 0·10 M Na_2CO_3 + 0.005% gelatin X = 1·464 at − 0·7 V *vs.* S.C.E.	
1·022	3·60	1·022	3·57
10·80	3·58	10·80	3·32
4. B.S.: 0·10 M Dien + 1·00 M NaOH + 0·005% gelatin X = 1·462 at −0·7 V *vs.* S.C.E.		12. B.S.: 0·10 M Dien + 1·00 M Na_2CO_3 + 0·005% gelatin X = 1·464 at − 0·7 V *vs.* S.C.E.	
1·022	3·37	1·022	2·81
10·80	3·40	10·80	2·82
5. B.S.: 0·02 M Trien + 0·10 M NaOH X = 1·637 at −0·8 V *vs.* S.C.E.		13. B.S.: 0·10 M Trien + 0·10 M Na_2CO_3 X = 1·445 at − 0·9 V *vs.* S.C.E.	
1·669	3·66	2·56	3·48
6·676	3·62	12·78	3·31
11·68	3·58	14. B.S.: 1·00 M Trien + 0·10 M Na_2CO_3 X = 1·431 at − 1·0 V *vs.* S.C.E.	
6. B.S.: 0·10 M Trien + 0·10 M NaOH X = 1·622 at −1·0 V *vs.* S.C.E.		2·56	2·75
0·755	3·50	12·78	2·62
3·776	3·44	15. B.S.: 0·10 M Trien + 1·00 M Na_2CO_3 X = 1·445 at − 0·9 V *vs.* S.C.E.	
9·440	3·45	2·56	2·75
7. B.S.: 0·02 M Trien + 1·00 M NaOH X = 1·622 at −1·1 V *vs.* S.C.E.		12·78	2·80
0·752	3·31	16. B.S.: 0·6 M Trien + 1·00 M NH_4Cl + 1·00 M NH_4OH X = 1·445 at − 0·9 V *vs.* S.C.E. (Second wave only)	
1·879	3·30	0·853	2·04
9·395	3·29	2·560	2·03
8. B.S.: 0·10 M Trien + 1·00 M NaOH X = 1·622 at −1·1 V *vs.* S.C.E.		5·120	2·03
0·752	3·21	12·80	2·02
1·879	3·24		
9·395	3·27		

* *Abbreviations.*—B.S.—base solution; X—$m^{2/3}\,t^{1/6}$ in $mg.^{2/3}\,sec.^{-1/2}$; Moen—Monoethanolamine; Dien—Diethanolamine; Trien—Triethanolamine.

obtained. As maxima appear in base solutions containing mono- and diethanolamines in presence of sodium hydroxide or carbonate at higher concentrations of copper, 0·005% gelatin has been incorporated in these solutions. Due to the complicated nature of the polarographic waves in presence of triethanolamine the diffusion current constant has been tested employing different concentrations of the amine. It can be seen that the constancy of the values of diffusion current constant is quite good indicating that the complexity of the wave does not affect the proportionality of the diffusion current with the concentration of copper in the case of these complexes.

In solutions containing ammonium chloride-ammonium hydroxide and triethanolamine, the diffusion current plateau of the first wave is flat only in solutions containing more than 0·6 M amine. However, it is difficult to compute the height of the first wave as the reduction starts even from the beginning. The diffusion current plateau of the second wave is well developed at all concentrations of the amine. As the measurement of the second wave depends for its accuracy on a perfectly flat first diffusion current, the effect of concentration of copper on the diffusion current constant has been tested in solutions containing 0·6 M triethanolamine. Figure 6 gives some of the polarograms obtained employing different concentrations of copper.

The constancy of the diffusion current constant in Table V shows that the various base solutions can be employed for the polarographic estimation of copper.

DISCUSSION

1. *Splitting of the polarographic wave.*—The splitting of the polarographic wave is quite prominent in solutions containing triethanolamine (Table I) while it is practically absent in mono- and diethanolamines. The splitting seems to be due to two species in sluggish equilibrium as noticed in the case of cadmium,[3] nickel[4] and cobalt.[5] At low pH values (5·3 and 6·5) it is reasonable to assume that the aquo-cupric ion is one species of the reducible ion as the half-wave potential is very close to that of aquo-cupric ion (— 0·01 V *vs.* S.C.E. in 1 N HNO_3). The increase in the half-wave potential beyond 6·5 may be due to a complex of the triethanolammonium ion with cupric ion. The second small wave noticed with increase in the alkali concentration (Fig. 2) can be explained to be due to a different complex containing more of the hydroxyl groups, since the concentration of the triethanolamine in the solutions has been maintained constant.

It is generally accepted[7] that Cu^{++} gets reduced *via* +1 state in ammoniacal solutions. In solutions containing mono- and diethanolamines in 1 M ammonium chloride and 1 M ammonia, the ratio of the heights of the two

waves (Table IV) is very nearly 1 at various concentrations of the amines indicating reduction *via* +1 state.

In triethanolamine solutions, however, the ratio between the heights of the two waves alters with a change in the concentration of triethanolamine (Table IV). To correspond to two independent one-electron steps, the ratio of the heights must be unity and should not alter much with the concentration of triethanolamine. In the present case, the ratio of the wave-heights first increases, remains constant and again increases. The change is far too large to be ascribed to different changes in the diffusion coefficients of the two complexes as the current is governed only by the diffusion coefficient of the cupric complex. It is very likely that reduction is not proceeding *via* +1 state but straight to the metallic state. Under these conditions, one has to conclude that the $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ values (0·045 V and 0·060 V for the first and the second waves), as being more due to two irreversible two-electron processes. Laitinen and Onstott[8] have given a similar explanation in copper-pyrophosphate system though Rogers and Reynolds[9] have mentioned that the reduction proceeds through +1 state.

2. *Effect of pH.*—Results presented in Table I indicate that except at pH 7, where triethanolamine shows a split wave, the behaviour of the three ethanolamine complexes at various pH values is substantially the same.

The shift in the half-wave potential at various pH values indicates the formation of two different complexes, one containing the amine and the other, the amine + hydroxyl (in highly alkaline solutions). It is noteworthy that in the cases where a doublet is formed the value of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ for each wave is about 0·030 V in non-ammoniacal solutions, confirming the view that the doublet is due to different species each getting reduced directly to the metallic state.

3. *Effect of concentration of the amine on the polarographic reversibility.*—With mono- and diethanolamines the wave is reversible at all concentrations of the amine while with triethanolamine the wave is reversible only at low concentrations of the amine (Tables II and III). As the concentration of triethanolamine is increased the value of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ of the polarographic wave increases indicating that very high activation energy is required for the reduction process in presence of high concentrations of triethanolamine. In the case of copper, only the triethanolamine complexes give irreversible waves in contradistinction to the behaviour of nickel[4] where both di- and triethanolamine complexes give irreversible waves and cobalt[5] where even some of the monoethanolamine complexes are irreversible.

The differences in the behaviour between the mono- and diethanolamine complexes on the one hand, and triethanolamine complexes on the other, appear to be due to the activated transfer of electron between the electrode and the ion in the case of triethanolamine which has three hydroxyl groups.

4. *Effect of the number of ethanol groups in the amine on the diffusion current constant.*—Reference to Table V indicates that the diffusion current constant decreases with the increase in the number of ethanol groups in the amine as in the case of cadmium.[3] This has to be interpreted as being due to a decrease in the diffusion coefficient of the complex with an increase in the number of ethanol groups in the amine.

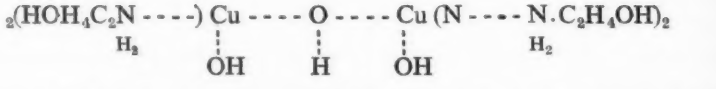
5. *Complex formation in presence of sodium hydroxide.*—It has already been stated that in solutions containing mono- and diethanolamines the reduction waves are reversible in character, while those in triethanolamine show varying degrees of reversibility. Application of Lingane's[3] equation shows that complexes formed have the following composition:

(i) $Cu_2(Moen)_4(OH)_3^+$

(ii) $Cu(Dien)_1(OH)_2$

(iii) $Cu(Dien)_2(OH)_2$

In the first complex it is likely that two cupric ions are linked to each other through the oxygen of the hydroxyl and the structure can be written as follows:



This type of linking has also been noticed previously.[10] In the case of diethanolamine it has been noticed that at lower and higher concentrations of the amine, one and two molecules of the amine co-ordinate with the cupric ion respectively. It is not possible to get an idea of the formula of the complex in triethanolamine solutions by an application of the equations for irreversible waves[6] due to progressive increase in the irreversibility with an increase in the concentration of triethanolamine.

6. *Complex formation in presence of sodium carbonate.*—The results presented in Table III suggest that carbonate ion does not enter the complex in contrast to the behaviour observed with cadmium.[3] The formula $Cu(Moen)_2^{++}$, $Cu(Moen)_3^{++}$, $Cu(Dien)_2^{++}$ are obtained by employing Lingane's equation.[3]

7. *Complex formation in presence of ammonium chloride and ammonium hydroxide.*—In these solutions, it is not possible to compute the number of ethanolamine groups that enter the complex as the half-wave potential is already shifted to a sufficiently negative potential and the amine may merely exchange with the ammonia in the complex.

8. *Thermodynamic data from polarographic measurements.*—The dissociation constant, Δ F°, *i.e.*, free energy for the dissociation of the complex and the standard potential for complex formation are calculated as described in a previous communication.[3] The half-wave potential of cupric ion has been taken to be + 0·010 V (*vs.* S.C.E.) at 30° C. The above value has been computed from the value for cupric ion in 1 N potassium nitrate given by Keefer[11] after applying temperature corrections.[12] The standard potential at 30° C. of the reduction reaction $Cu^{++} + 2e = Cu$ has been taken as + 0·340 V (*vs.* N.H.E.).[13]

(i) *Cu_2 (Moen)$_4$ (OH)$_3^+$.*—

$Cu_2(Moen)_4(OH)_3^+ \rightarrow 2\,Cu^{++} + 4\,Moen + 3\,OH^-$

$K_d = 9{\cdot}33 \times 10^{-19}$; Δ F° = + 25·04 Kilocals.

$2\,Cu + 4\,Moen + 3\,OH^- \rightarrow Cu_2(Moen)_4(OH)_3^+ + 4\,e$;

Standard potential = + 0·202 V (*vs.* N.H.E.).

(ii) *Cu (Dien)$_1$ (OH)$_2$.*—

$Cu(Dien)_1(OH)_2 \rightarrow Cu^{++} + Dien + 2\,OH^-$

$K_d = 6{\cdot}46 \times 10^{-19}$; Δ F° = + 23·26 Kilocals.

$Cu + Dien + 2\,OH^- \rightarrow Cu(Dien)_1(OH)_2 + 2\,e$;

Standard potential = + 0·207 V (*vs.* N.H.E.).

(iii) *Cu (Dien)$_2^{++}$.*—

$Cu(Dien)_2^{++} \rightarrow Cu^{++} + 2\,Dien$

$K_d = 3{\cdot}16 \times 10^{-15}$; Δ F° = + 20·14 Kilocals.

$Cu + 2\,Dien \rightarrow Cu(Dien)_2^{++} + 2\,e$;

Standard potential = + 0·096 V (*vs.* N.H.E.).

The results recorded in the present paper indicate the existence of $Cu_2(Moen)_4(OH)_3^+$, $Cu(Dien)_1(OH)_2$, $Cu(Dien)_2(OH)_2$ and $Cu(Moen)_2^{++}$ in addition to $Cu(Moen)_3^{++}$ and $Cu(Dien)_2^{++}$ reported by Hieber and Levy.[2] In addition to the above, evidence has also been obtained for the formation of complex in presence of triethanolamine, which could not be isolated by Hieber and Levy due to the high syrupy nature of the solutions.

SUMMARY

1. The polarographic behaviour of copper-ethanolamine complexes has been studied at various pH values and also employing the following alkaline reagents, namely, sodium hydroxide, sodium carbonate and ammonium chloride-ammonium hydroxide.

2. It has been noticed that the reduction process is essentially reversible in presence of mono- and diethanolamines and irreversible with triethanolamine.

3. The phenomenon of split wave has been noticed only in solutions containing triethanolamine and non-ammoniacal alkaline reagents. In ammoniacal solutions the split waves are noticed with all the three amines. These observations have been suitably accounted for.

4. The formation of the following complexes is deduced from the polarographic data:

$Cu_2(Moen)_4(OH)_3^+$	$Cu(Moen)_2^{++}$	$Cu(Moen)_3^{++}$
$Cu(Dien)_1(OH)_2$	$Cu(Dien)_2(OH)_2$	$Cu(Dien)_2^{++}$

Moen and Dien represent monoethanolamine and diethanolamine respectively.

5. It has been concluded that ethanolamine complexes of copper can be employed for analytical estimation of copper.

6. Thermodynamic constants have been calculated from polarographic data in systems giving rise to reversible reduction processes.

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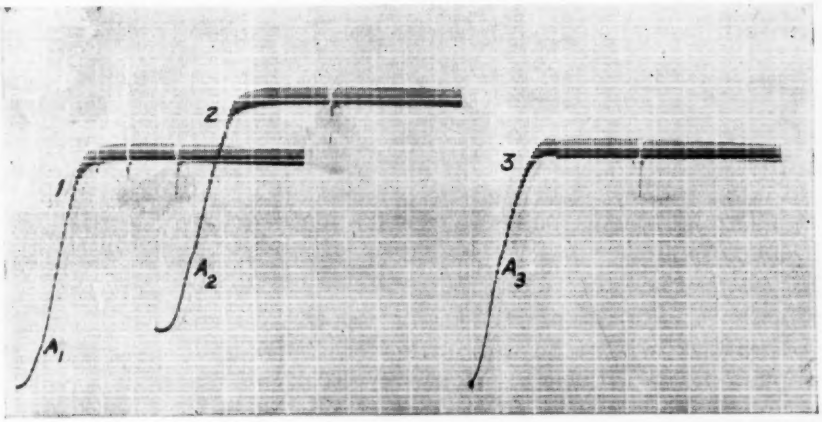

FIG. 1. Effect of pH on the polarographic behaviour of copper (2·560 millimolar) in triethanolamine. Curves 1, 2 and 3 have been taken at pH 7·20, 6·50 and 5·40 respectively. Sensitivity : *s*/100.

The voltage lines just before the beginning of the polarograms correspond to 0·027, 0·127 and 0·127 V *vs.* S.C.E.

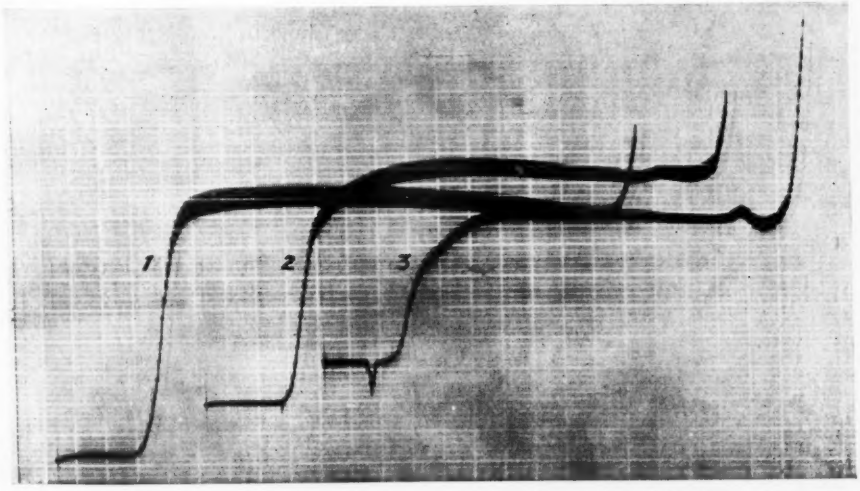

FIG. 2. Effect of sodium hydroxide on the polarographic behaviour of copper (1·669 millimolar) in triethanolamine. Curves 1, 2 and 3 have been taken in base solutions containing 0·02 M triethanolamine and 0·10, 1·00 and 5·00 M sodium hydroxide respectively. Sensitivity : *s*/70.

The voltage lines just before the beginning of the various polarograms correspond to − 0·073, − 0·173 and − 0·273 V *vs.* S.C.E.

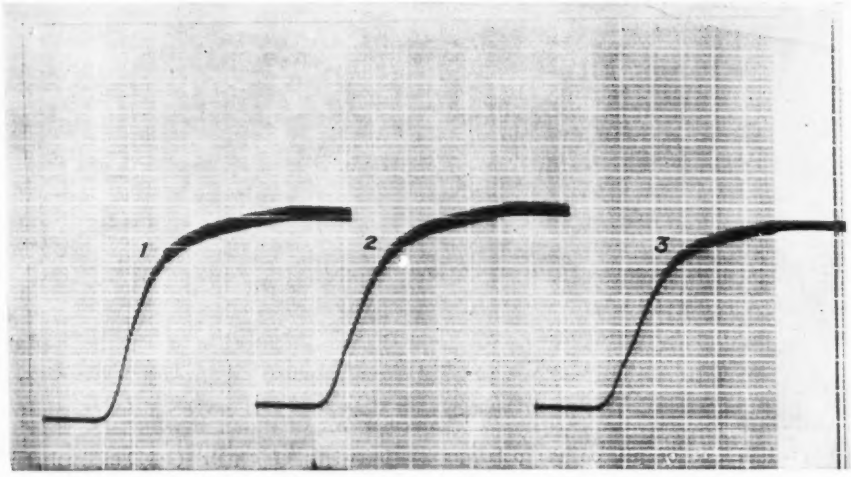

FIG. 3. Effect of sodium hydroxide (0·1 M) on the polarographic behaviour of copper (1·888 millimolar) in triethanolamine. Curves 1, 2 and 3 have been taken in base solutions containing 0·10, 0·50 and 0·70 M triethanolamine respectively. Sensitivity : *s*/70.

The voltage line preceding each polarogram corresponds to — 0·273 V *vs.* S.C.E.

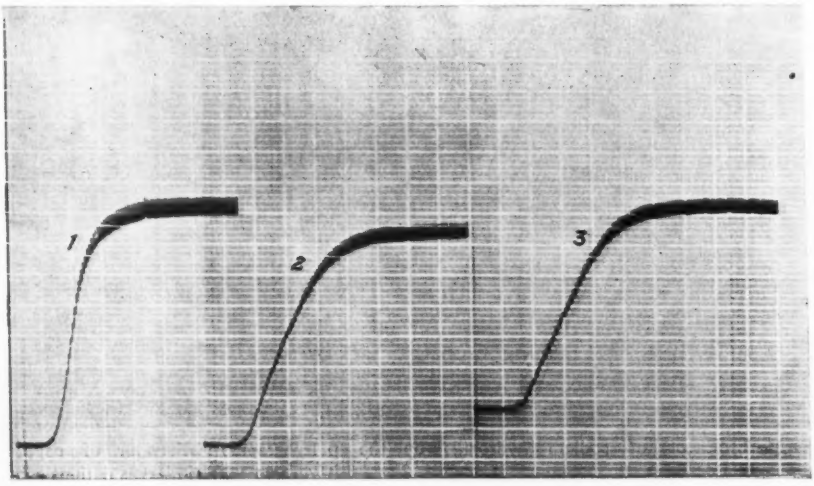

FIG. 4. Effect of sodium hydroxide (1·0 M) on the polarographic behaviour of copper (1·888 millimolar) in triethanolamine. Curves 1, 2 and 3 have been taken in solutions containing 0·30, 0·50 and 0·70 M triethanolamine respectively. Sensitivity : *s*/70.

The voltage line preceding each polarogram corresponds to — 0·273 V *vs.* S.C.E.

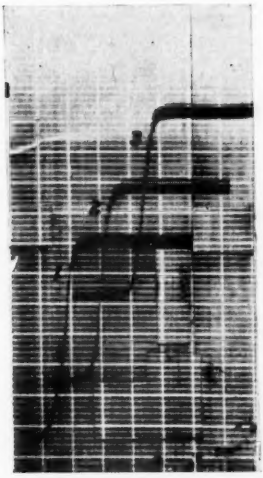

FIG. 5. Effect of sodium hydroxide (1·0 M) on the polarographic behaviour of copper (1·022 millimolar) in monoethanolamine. Curves 1, 2 and 3 have been obtained in solutions containing 0·02, 0·10 and 0·50 M monoethanolamine respectively. Sensitivity : *s*/50.

The voltage line just before the beginning of the polarograms correspond to — 0·173, — 0·273 and — 0·273 V *vs.* S.C.E. respectively.

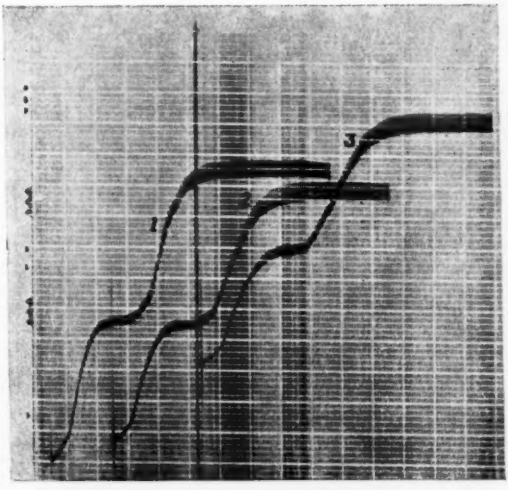

FIG. 6. Polarograms of copper in ammonium chloride (1·0 M), ammonium hydroxide (1·0 M). Curves 1–3 are obtained with 0·853, 5·120 and 12·80 millimolar copper the sensitivities being *s*/30, *s*/200 and *s*/500 respectively.

The voltage line preceding each polarogram corresponds to — 0·073 V *vs.* S.C.E.

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ERRATA

Volume XLVI, No. 4

On page 296, in Equation (20) *read* k^2 *for* K^2.

On page 297, in the third line from the bottom *read* k_1, k_2 *for* K_1, K_2.

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CONTENTS

PAGE

The Heat Capacity of Diamond between 0 and 1000° K. Sir C. V. Raman 323

Distribution of Radioactivity in the Rocks of South India. Part IV. Fluorine-Bearing Granites of Podili-Kanigiri Area and Associated Rocks . . . . . C. Mahadevan and A. V. R. Sastry 333

A Synthesis of Stillopsidin and Its Methyl Ethers . . . . . K. R. Laumas, S. Neelakantan and T. R. Seshadri 343

The Intermediate Layer of Stratification ($F_{1\cdot5}$) between F_1 and F_2 at Ahmedabad . . . . . K. M. Kotadia 349

A Modified Gating Logic to Improve the Speed of Operation of Double Rank Counters . . . . . B. K. Basu and P. V. S. Rao 354

Studies with Scintillation Coincidence Spectrometer: Se^{75} and Sb^{125} . . . . . Girish Chandra 360

Characteristic Roots of the Product of Certain Matrices . . . N. A. Khan 367

On a Function of Ramanujan . . . . . Omar Ali Siddiqi 371

Polarographic Behaviour of Metals in Ethanolamines. Part V. Copper . . . . . R. S. Subrahmanya 377